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TRANSITION METAL CARBONYLS OF SILICON

by



JAMES KOICHI HOYANO

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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The undersigned certify that they have read, and  
recommend to the Faculty of Graduate Studies for  
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submitted by JAMES KOICHI HOYANO, in partial ful-  
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Doctor of Philosophy.





# A B S T R A C T

Various silicon-transition metal carbonyl derivatives have been synthesized by thermal and photochemical reactions of silicon hydrides with metal carbonyls. The infrared, nmr and mass spectral properties were studied and revealed various structural and bonding aspects of these complexes.

The thermal reactions of the difunctional silanes  $R_2SiH_2$  (where R is Cl,  $CH_3$ ,  $C_6H_5$ ) with the carbonyls of manganese, rhenium, iron and cobalt yielded polynuclear transition metal-silicon species such as  $R_2Si[Mn(CO)_5]_2$ ,  $[R_2SiRe(CO)_4]_2$ ,  $(R_2Si)_3Fe_2(CO)_6$ , and  $R_2SiCo_2(CO)_7$ . The structures were assigned mainly from the infrared spectra.

The photochemical reactions of  $R_2SiH_2$  (where R is  $CH_3$ ,  $C_2H_5$ ,  $C_6H_5$ ) with the carbonyls of rhenium, tungsten and molybdenum yielded various silicon-bridged dinuclear metal complexes of the types  $R_2SiH_2Re_2(CO)_8$ , 1,  $(R_2SiH_2)_2Re_2(CO)_6$ , 2,  $(R_2Si)_2H_2Re_2(CO)_7$ , 3,  $R_2SiW_2(CO)_{10}$ , 4,  $(R_2Si)_2W_2(CO)_{10}$ , 5, and  $(R_2Si)_2H_2W_2(CO)_8$ , 6. The spectroscopic properties of the complexes indicated the most likely structures; a possible location of the hydride ligands in bridging positions between the transition metal and silicon is suggested for compounds 1, 2, 3 and 6. During the course of these reactions the complexes  $H_2Re_2(CO)_8$  and  $HClRe_2(CO)_8$  were also obtained; their properties indicate hydrogen bridges between two rhenium



atoms.

The compounds  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  (where R is methyl or phenyl) were obtained from the photochemical reaction of  $\text{Re}_2(\text{CO})_{10}$  with the appropriate silane. These derivatives can be best formulated with linear Re-H-Re bridged systems.

A number of silicon derivatives of  $\text{CpM}(\text{CO})_3$  ( $\text{Cp} = \pi\text{-C}_5\text{H}_5$ ,  $\text{M} = \text{Mn}, \text{Re}$ ) have been prepared photochemically; these have the general formula  $\text{R}_3\text{SiHM}(\text{CO})_2\text{Cp}$ . Treatment of cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  ( $\text{Ph} = \text{C}_6\text{H}_5$ ) with ethanolic KOH gave  $[\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  which on reprotonation yielded trans- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ . Other reactions of the anion also gave trans products. The compound  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  was obtained from the ultraviolet irradiation of  $\text{CpRe}(\text{CO})_3$ .

Some iron-tin complexes  $\text{R}_{3-n}\text{X}_n\text{SnFe}(\text{CO})_2\text{Cp}$  (where X = halogen, R = alkyl or aryl,  $n = 0, 1, 2, 3$ ) were synthesized; the complexes with different groups on the tin were found to exhibit conformational isomerism.



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CHAPTER II N T R O D U C T I O N

The study of complexes containing direct covalent bonds between a main group metal and a transition metal has grown immensely in the last 10 - 15 years. Specifically pertinent to the work to be presented here are the complexes involving the main group IV metals silicon, germanium, tin and lead bonded to a transition metal where the transition metal moiety is a metal carbonyl or a metal carbonyl derivative. (Although silicon is not usually classified as a metal, its properties and methods of preparation in compounds of the types to be discussed are similar to germanium, tin and lead. Therefore, any reference made to group IV metals in general will apply also to silicon in this thesis). Research in this area has been focussed mainly on the transition metals chromium, manganese, iron, cobalt and to a slightly lesser extent their respective second and third row congeners. This is probably due to the ready availability of the binary carbonyls and their derivatives. Of the group IV metals, examples of tin and germanium derivatives are the most numerous. Examples of lead transition-metal carbonyl complexes are fewer probably because of their low thermal stabilities. Up to the last three or four years only a few examples of silicon-transition metal bonds were known. It now appears that this was due mainly to the lack of suitable synthetic methods.



This treatise will present the preparation and properties of some transition metal carbonyl derivatives of silicon and tin and of some related complexes. The first and major portion (Chapters II-V) will relate the preparation and properties of various silicon derivatives of transition metal carbonyls. From this and other studies carried out in this laboratory, <sup>1</sup> the reaction of silicon hydrides with metal carbonyls under various conditions has been found to be a general method for preparing silicon-transition metal bonds. A number of novel silicon-transition metal complexes (mainly of manganese and rhenium) were obtained and will be described. The last Chapter (VI) will describe the synthesis and spectral properties of some iron-tin species of the type  $R_{3-n}X_nSn-Fe(CO)_2Cp$  ( $n = 0, 1, 2, 3$ ).

A brief outline of the properties and syntheses of main group IV metal-transition metal bonded complexes is now given in relation to the work to be presented.





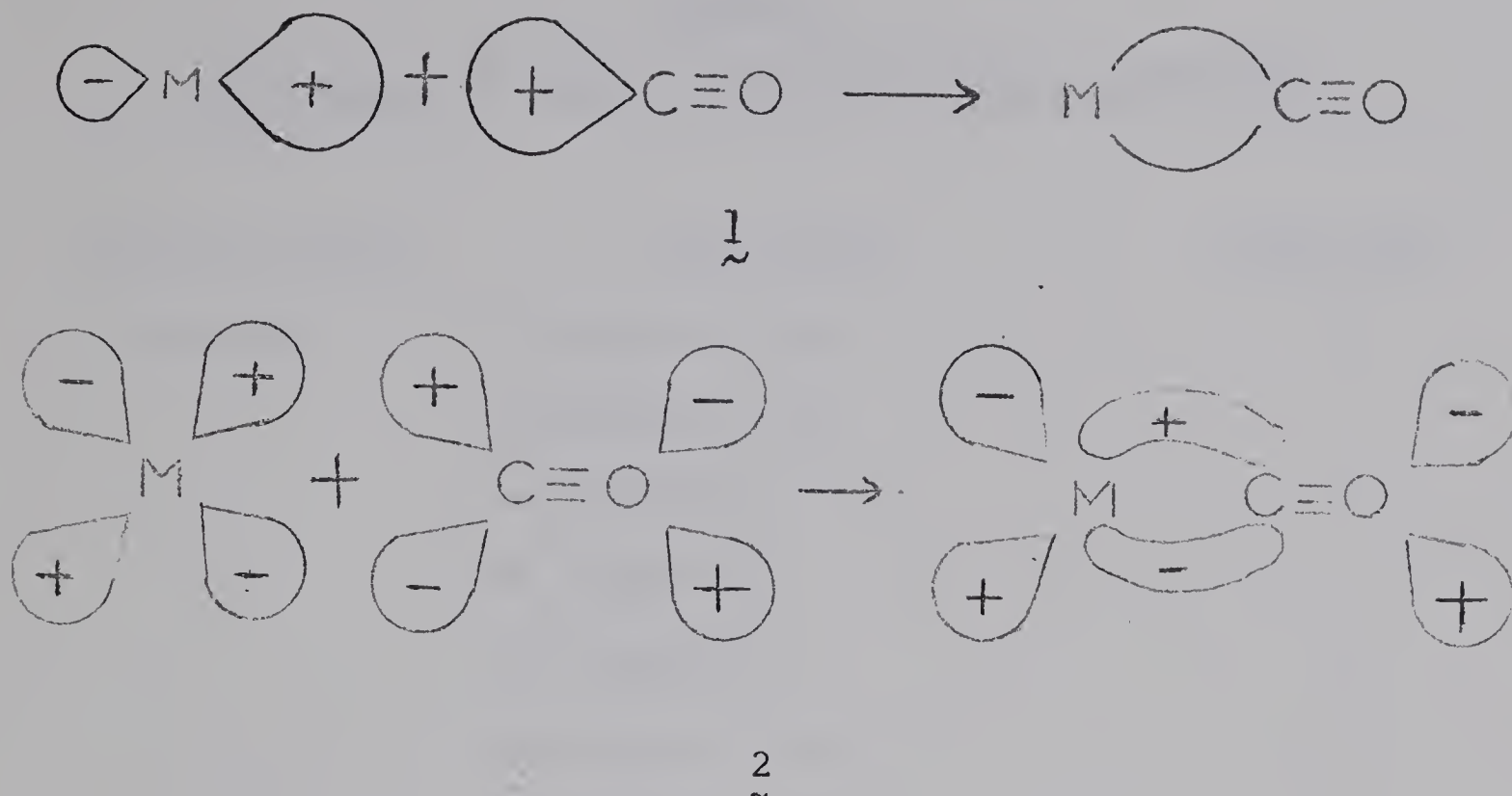
A. GENERAL ASPECTS OF GROUP IV METAL-TRANSITION METAL COMPLEXES.

Although the first group IV metal-transition metal bonded complexes were prepared in the early 1940's,<sup>2,3,4,5</sup> only in the last 10-15 years have these complexes been fully characterized with the aid of modern physical methods. Closely related to the substantiation of group IV metal-transition metal covalent bonds was the establishment of definite covalent metal-metal bonds between transition metals. In many of the complexes known today both types of metal-metal bonds are present in the same molecule.

In most stable compounds containing metal-metal bonds of the two types mentioned above, a requisite appears to be the stabilization of the transition metal in a low formal oxidation state. This stabilization is usually accomplished by such ligands as carbon monoxide, tertiary phosphines, tertiary arsines and various cyclic olefins. The stability of the transition-metal carbonyls and their derivatives, for example, is generally attributed to the synergic effect of the  $\sigma$  and  $\pi$  bonds.<sup>6,7</sup> A molecular orbital picture of this effect is shown in 1 and 2; the appropriate atomic and molecular orbitals suitable for overlap are shown.

The metal-carbon bond can be thought of as formed by the following sequence: formation of a sigma bond by donation of the carbon lone pair to an empty metal hybrid





orbital 1, then back donation from the filled metal d orbitals of appropriate symmetry into the empty antibonding  $\pi^*$  orbitals of CO 2. The  $\pi$  bonding removes the excess charge built up on the metal by the sigma donation. The net effect is that a stronger bond is produced than the sum of the two effects separately; hence, the term synergic. The binary carbonyls such as  $\text{W}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}(\text{CO})_5$  and  $\text{Co}_2(\text{CO})_8$ , which are common starting materials in the syntheses of group IV metal-transition metal carbonyl complexes, are all considered to have the transition metal in the zero oxidation state.

Many of the possible combinations of transition metal carbonyls or their derivatives bonded to the elements silicon, germanium, tin and lead are now known. This is illustrated by the examples given in Table 1. The transition



TABLE I  
SOME GROUP IV METAL-TRANSITION METAL COMPOUNDS

<u>Group IV Metal</u>	<u>Compound*</u>	<u>Reference</u>
Silicon	$\text{Cl}_3\text{Si}\underline{\text{Cr}}(\text{CO})_3\text{Cp}$	8
	$\text{Cl}_3\text{Si}\underline{\text{Mo}}(\text{CO})_3\text{Cp}$	8
	$\text{Me}_3\text{Si}\underline{\text{W}}(\text{CO})_3\text{Cp}$	9
	$\text{Ph}_3\text{Si}\underline{\text{Mn}}(\text{CO})_5$	10
	$\text{Cl}_3\text{Si}\underline{\text{Re}}(\text{CO})_5$	8
	$\text{Me}_3\text{Si}\underline{\text{Fe}}(\text{CO})_2\text{Cp}$	11
	$[\text{Me}_3\text{Si}\underline{\text{Ru}}(\text{CO})_4]_2$	12
	$\text{Cl}_3\text{Si}\underline{\text{Co}}(\text{CO})_4$	13
	$\text{Cl}_3\text{Si}\underline{\text{Rh}}\text{H}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	14
	$\text{Cl}_3\text{Si}\underline{\text{Ir}}\text{H}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	15
	$\text{Cl}_3\text{Si}\underline{\text{Ni}}(\text{CO})\text{Cp}$	8
Germanium	$\text{Ph}_3\text{Ge}\underline{\text{Cr}}(\text{CO})_3\text{Cp}$	16, 17
	$\text{Cl}_3\text{Ge}\underline{\text{Mo}}\text{Cl}(\text{CO})_3\text{bipy}$	18
	$\text{I}_2\text{Ge}[\underline{\text{W}}(\text{CO})_5]_2^-$	19
	$\text{Cl}_3\text{Ge}\underline{\text{Mn}}(\text{CO})_5$	20
	$\text{Ph}_2\text{Ge}[\underline{\text{Re}}(\text{CO})_5]_2$	21
	$\text{Ph}_2\text{Ge}\underline{\text{Fe}}_2(\text{CO})_8$	22
	$\text{I}_2\text{Ge}[\underline{\text{Ru}}(\text{CO})_2\text{Cp}]_2$	23
	$\text{I}_3\text{Ge}\underline{\text{Co}}(\text{CO})_2\text{Cp}$	24
Tin	$\text{Ph}_3\text{Sn}\underline{\text{Cr}}(\text{CO})_3\text{Cp}$	17
	$\text{Me}_2\text{Sn}[\underline{\text{Mo}}(\text{CO})_3\text{Cp}]_2$	17



TABLE I (continued)

<u>Group IV Metal</u>	<u>Compound</u>	<u>Reference</u>
Tin	$\text{Cl}_2\text{Sn}[\underline{\text{W}}(\text{CO})_3\text{Cp}]_2$	16
	$\text{Ph}_3\text{Sn}\underline{\text{Mn}}(\text{CO})_5$	25
	$\text{Cl}_2\text{Sn}[\underline{\text{Re}}(\text{CO})_5]_2$	26
	$[\text{Me}_2\text{Sn}\underline{\text{Fe}}(\text{CO})_4]_2$	27
	$(\text{Ph}_3\text{Sn})_2\underline{\text{Ru}}(\text{CO})_4$	28
	$\text{Cl}_3\text{Sn}\underline{\text{OsH}}(\text{CO})_4$	29
	$\text{Cl}_3\text{Sn}[\underline{\text{Co}}(\text{CO})_4]_3$	30
	$\text{Me}_3\text{Sn}\underline{\text{Rh}}(\text{CO})_2(\text{PPh}_3)_2$	31
	$\text{Cl}_3\text{Sn}\underline{\text{IrCl}}_2(\text{CO})(\text{PPh}_3)_2$	32
	$\text{Cl}_2\text{Sn}[\underline{\text{Ni}}(\text{CO})\text{Cp}]_2$	33
Lead	$\text{Ph}_3\text{Pb}\underline{\text{Cr}}(\text{CO})_3\text{Cp}$	16, 17
	$\text{Ph}_3\text{Pb}\underline{\text{Mo}}(\text{CO})_3\text{Cp}$	16, 17
	$\text{Ph}_3\text{Pb}\underline{\text{W}}(\text{CO})_3\text{Cp}$	16, 17
	$\text{Me}_3\text{Pb}\underline{\text{Mn}}(\text{CO})_5$	25
	$\text{Ph}_3\text{Pb}\underline{\text{Re}}(\text{CO})_5$	10, 34
	$\text{Pb}[\underline{\text{Fe}}(\text{CO})_4]_4$	27
	$\text{Ph}_2\text{Pb}[\underline{\text{Co}}(\text{CO})_4]_2$	35

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\* In this table, and throughout this work the following abbreviations will be employed: Me = CH<sub>3</sub>, Et = C<sub>2</sub>H<sub>5</sub>, n-Bu = n-C<sub>4</sub>H<sub>9</sub>, Ph = C<sub>6</sub>H<sub>5</sub>, Cp = π bonded cyclopentadienyl group, bipy = 2,2'-bipyridyl, diphos = 1,2-bis(diphenylphosphino)ethane.





metal which is covalently bonded to the group IV element is underlined in this table.

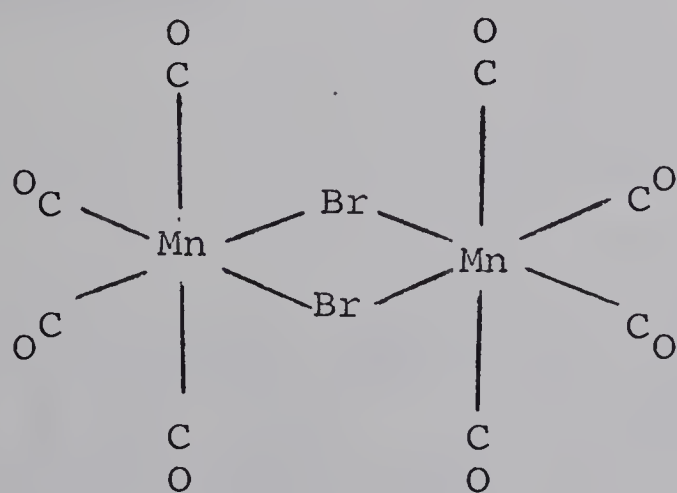
Most of the compounds in Table I are moderately air-stable crystalline solids. The complex  $\text{Cl}_2\text{Sn}[\text{Re}(\text{CO})_5]_2$ <sup>26</sup> melts at 171-172° without decomposition and appears stable in air for long periods of time while the complex  $\text{Cl}_3\text{SiHFe}(\text{CO})_4$ <sup>67</sup> is a very air-sensitive liquid. Most of the compounds fall between these two extremes. Generally the preparation and reactions of the group IV metal-transition metal bonded compounds are carried out under an inert nitrogen atmosphere.

The effective atomic number rule or noble-gas formalism is a valuable concept in predicting the stoichiometries and structures of transition metal carbonyls and their derivatives. This formalism requires that the number of valence electrons possessed by the transition metal in the zerovalent state plus the number of electrons contributed by the ligands equals the number of electrons in the succeeding noble-gas atom. Ligands such as carbon monoxide, olefins, tertiary phosphines and tertiary arsines are considered to be two electron donors. Covalent single bonds to other transition metals, to main group metals, to hydrogen and to halogens are all considered to contribute one electron per bond. A halogen, phosphorus or sulfur bridging two transition metals supplies three electrons. Pi-bonded benzene and cyclopentadienyl rings are considered to supply six and five electrons respectively. Most transition metal compounds obey this rule as can be seen

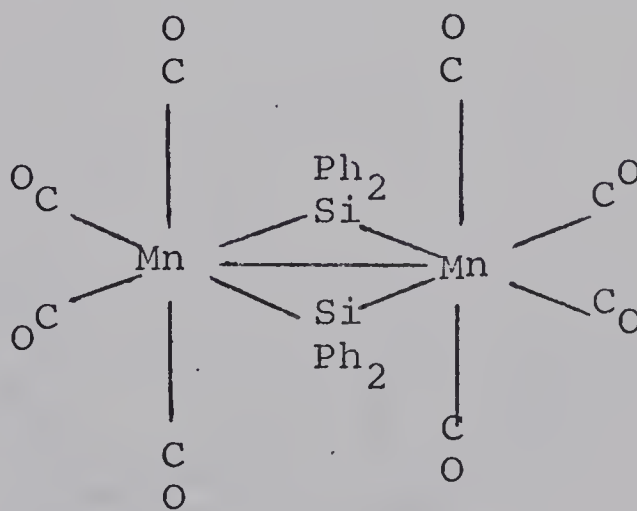


from the examples in Table I. There are some rhodium and iridium complexes known which do not conform to the effective atomic number rule. However, it appears that almost all the known transition metal carbonyls and their derivatives do conform to the effective atomic number rule for the chromium, manganese and iron groups. In fact the faith of chemists is so great that metal-metal bonds by electron sharing have been proposed in order to maintain the EAN rule.

The utility of the effective atomic number rule is illustrated by the complexes  $[\text{BrMn}(\text{CO})_4]_2$ <sup>36,37</sup> and  $[\text{Ph}_2\text{SiMn}(\text{CO})_4]_2$ <sup>1</sup>. The infrared spectra in the carbonyl stretching region suggested a similar  $D_{2h}$  structure for both complexes as shown in 3 and 4.



3



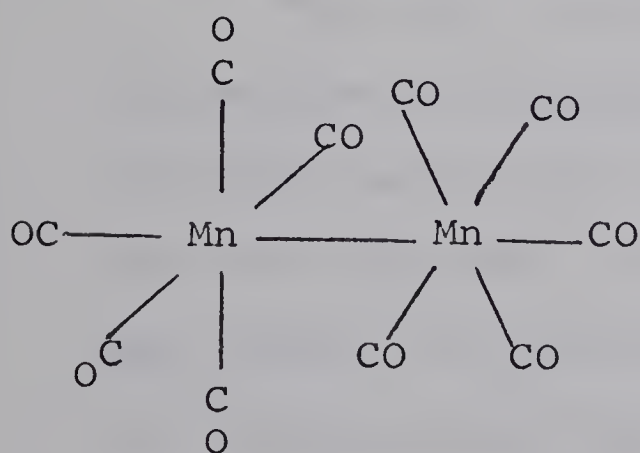
4

The effective atomic number rule predicts no metal-metal bond for 3 and a single manganese-manganese bond for

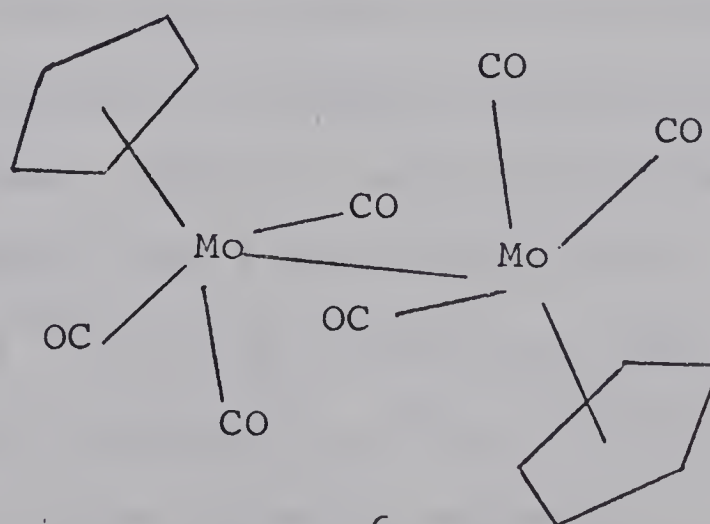


4. The X-ray crystal structures supported the overall  $D_{2h}$  molecular symmetry for both compounds. The Mn-Mn distance in  $[\text{BrMn}(\text{CO})_4]_2$  was  $3.74 \text{ \AA}$ <sup>38</sup> while the Mn-Mn length in  $[\text{Ph}_2\text{SiMn}(\text{CO})_4]_2$  was  $2.87 \text{ \AA}$ .<sup>39</sup> The latter distance is in good agreement with the Mn-Mn single bond length of  $2.92 \text{ \AA}$  in  $\text{Mn}_2(\text{CO})_{10}$ .<sup>40</sup>

X-ray crystallography is probably the most direct and definitive method of determining molecular structures and the existence of metal-metal bonds. The unambiguous existence of covalent bonds between transition metals was first shown in 1957 by the structure determinations of  $\text{Mn}_2(\text{CO})_{10}$  by Dahl and Rundle<sup>40</sup> and  $[\text{CpMo}(\text{CO})_3]_2$  by Wilson and Shoemaker.<sup>41</sup> The structures showed non-bridged metal-metal bonds with distances of  $2.92 \text{ \AA}$  (Mn-Mn) and  $3.22 \text{ \AA}$  (Mo-Mo) respectively.



5



6





The first X-ray evidence for a covalent group IV metal-transition metal bond was in the structure of  $\text{Ph}_3\text{SnMn}(\text{CO})_4\text{PPh}_3$  by Bryan<sup>42</sup> in 1964. This was closely followed by Kilbourn and Powell with the structure of  $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ .<sup>43</sup>

The covalent metal radii obtained from the structure determinations of 5 and 6 are appreciably larger than Pauling radii.<sup>45</sup> From the structure determination of a related molybdenum compound  $\text{EtMo}(\text{CO})_3\text{Cp}$  and other related work Bennett and Mason first suggested a rationale for the longer metal radii in the carbonyl compounds.<sup>207,208</sup> Since the initial studies, the structures of an increasing number of related compounds have been determined and many single bond covalent radii are now available. Some typical transition metal radii for the carbonyls are given in Table II. These values were derived from selected non-bridged metal-metal distances, if available.

The radii in Table II are only guides and vary with the particular compound especially if bridging groups across the metal-metal bond are present. This is especially true for iron complexes. For example, the tin-bridged Fe-Fe bond length in  $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ <sup>7 50</sup> is 2.87 Å while the carbonyl-bridge Fe-Fe bond length in  $\text{Fe}_3(\text{CO})_{12}$ <sup>46</sup> is 2.55 Å. However, the values in Table II are reliable guides in determining whether a metal-metal bond exists. For example,





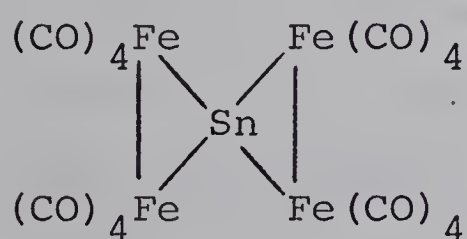
TABLE IISOME COVALENT RADII OF TRANSITION METALS

<u>Transition Metal</u>	<u>Metal Carbonyl Radii</u>	<u>Pauling Radii</u> <sup>45</sup>
Cr	1.50 Å <sup>44</sup>	1.18 Å
Mo	1.61 <sup>41</sup>	1.30
Mn	1.46 <sup>40</sup>	1.17
Tc	1.51 <sup>44</sup>	1.27
Re	1.51 <sup>40</sup>	1.28
Fe	1.35 <sup>46</sup>	1.17
Ru	1.42 <sup>47</sup>	1.25
Os	1.44 <sup>48</sup>	1.26
Co	1.26 <sup>49</sup>	1.16

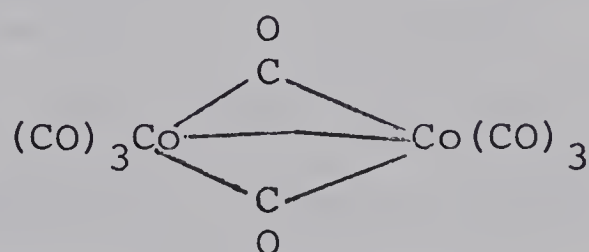
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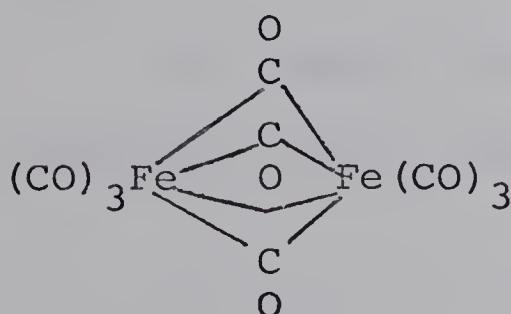
the binary carbonyls  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}_2(\text{CO})_9$  are now generally accepted to have metal-metal bonds as predicted by the E.A.N. rule. The X-ray structures of 8 and 9 showed that both complexes contained bridging carbonyls with Co-Co and Fe-Fe distances of  $2.52 \text{ \AA}$ <sup>49</sup> and  $2.46 \text{ \AA}$ <sup>51</sup> respectively. Both distances are in the region normally associated with metal-metal bonds. Note that the structure of  $\text{Fe}_2(\text{CO})_9$  was determined in 1939. When a metal-metal bond is not present, the metal-metal distances are usually much greater; from the X-ray structure of  $\text{Me}_4\text{Sn}_3\text{Fe}_4(\text{CO})_{16}$ <sup>52</sup> 10 the E.A.N. rule requires no Fe-Fe bonds and the shortest Fe-Fe distances are  $3.87 \text{ \AA}$ <sup>52</sup> which is much too long for a metal-metal bond.



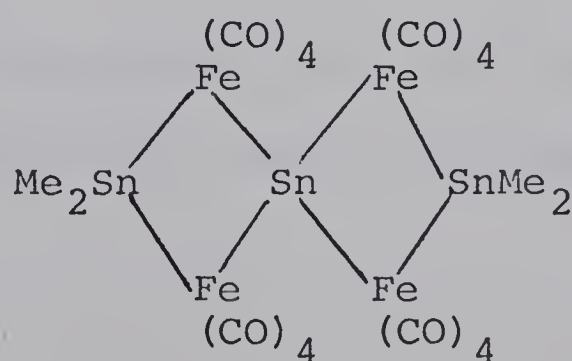
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8



9



10



A recent review by Abel and Stone<sup>53</sup> summarizes the structural aspects of the transition metal carbonyls and their derivatives. Numerous examples of the type given above can be found in this review. The following chapters in this thesis will also discuss some examples of the variation of metal-metal bonded distances.

The spectroscopic tools of infrared, nuclear magnetic resonance, and mass spectra are indispensable in the study of transition metal carbonyls and their derivatives and will be elaborated on in the appropriate sections of the thesis. The carbonyl stretching region of the infrared spectrum is probably the single most potent spectroscopic area when studying carbonyls and their derivatives. The carbonyl stretching band positions, relative intensities, and number of bands can all be used to make structural inferences. Together with other spectroscopic and physical data and from the knowledge of related compounds, the most likely structures of new compounds can usually be predicted. This will be illustrated for some of the compounds in this work.

The general methods of synthesizing group IV metal-transition metal bonded complexes will now be discussed.



B. SYNTHESIS OF GROUP IV METAL-TRANSITION METAL BONDS.

The reactions employed in synthesizing main group IV metal-transition metal bonds can usually be placed in one of five general categories;

- (1) displacement of halide ions by metal carbonyl anions.
- (2) insertion reactions.
- (3) elimination of neutral molecules.
- (4) oxidative additions.
- (5) oxidative eliminations.

These reactions are applicable to main group metals in general, but the discussion here will be restricted to the group IV metals. A recent review by Stone<sup>54</sup> gives a summary of the synthetic methods employed in metal-metal bonded complexes. Some reactions can be placed under more than one category and in these cases the choice has been arbitrary. The classification of the reactions has no mechanistic implications and is based solely on the net results of the reactions. Each of the complexes listed in Table I was synthesized by one of the above methods. Some examples of each method are now given.

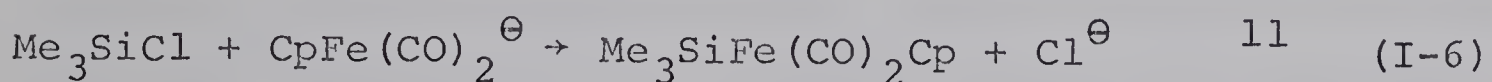
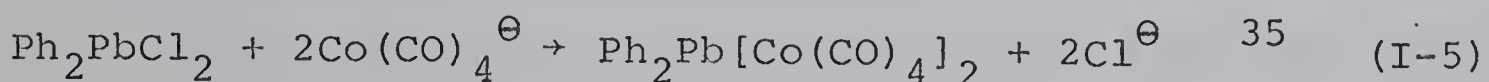
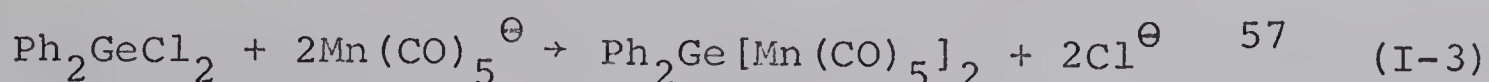
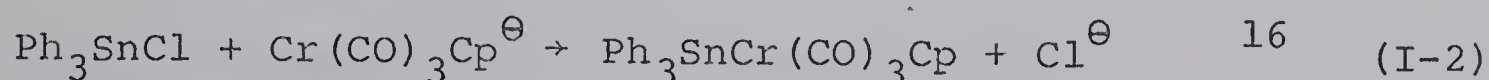
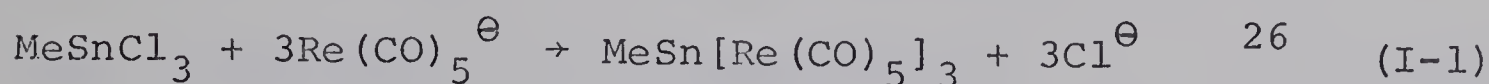
1. Displacement of halide ions by metal carbonyl anions.

This method has been used extensively in the synthesis of numerous germanium, tin and lead derivatives of the transition metal carbonyls. The generation of the metal carbonyl





anions is well established and detailed accounts can be found in reviews by Wender and Pino<sup>55</sup> and by King.<sup>56</sup> Some examples of these displacement reactions are shown below.

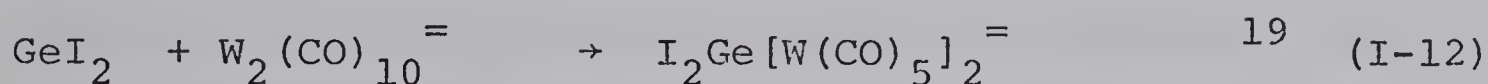
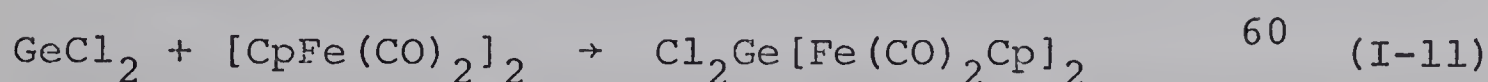
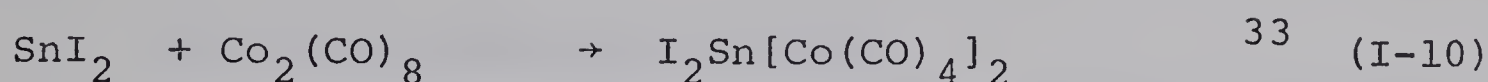
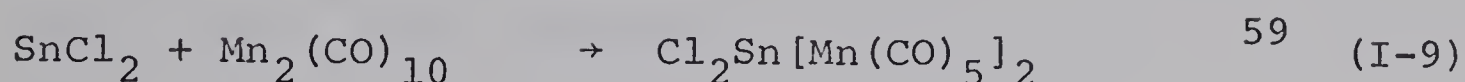
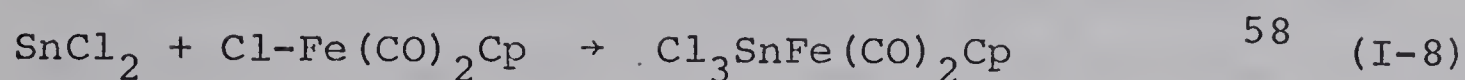
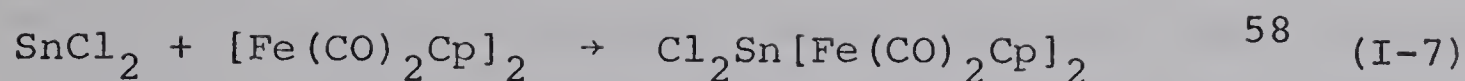


The last example (I-6) is one of the few silicon-transition metal carbonyl complexes which has been synthesized by halide displacement. It has been found that the displacement reaction is not general for the synthesis of transition metal-silicon bonds.<sup>10</sup>

## 2. Insertion reactions.

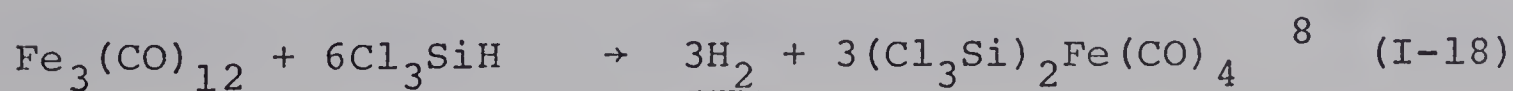
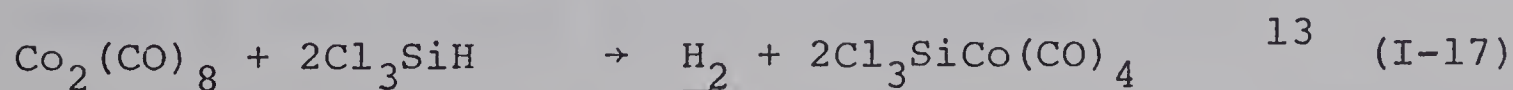
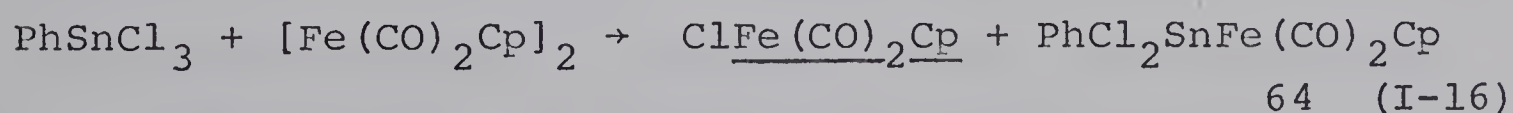
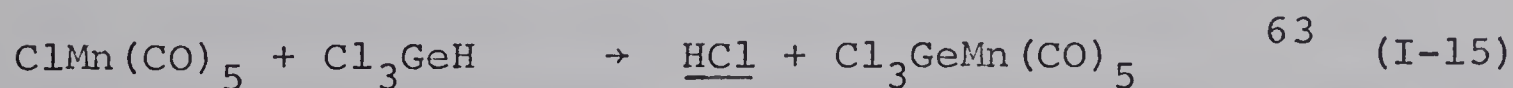
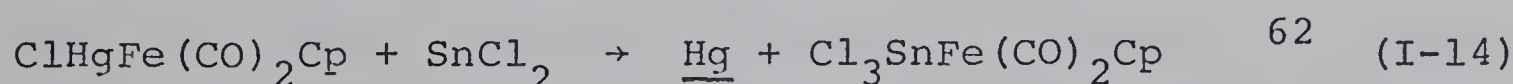
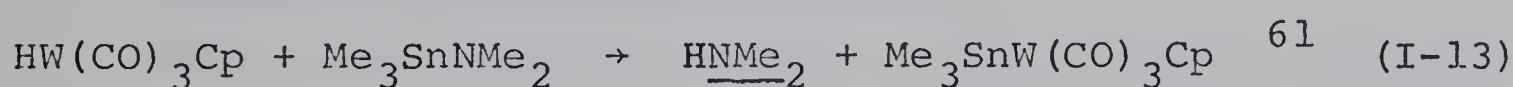
In syntheses of this type a germanium(II) or tin(II) halide reacts with a transition metal carbonyl derivative so that the net result is an insertion into a metal-metal or a metal-halogen bond. The tin or germanium is then formally in the IV oxidation state. Illustrations of some insertion reactions are given below.





### 3. Elimination of a neutral molecule(s).

These reactions refer to the various reactions where a group IV metal-transition metal bonded species is formed with the 'elimination' of a neutral molecule or molecules. The elimination of an assortment of neutral molecules can occur as shown below.



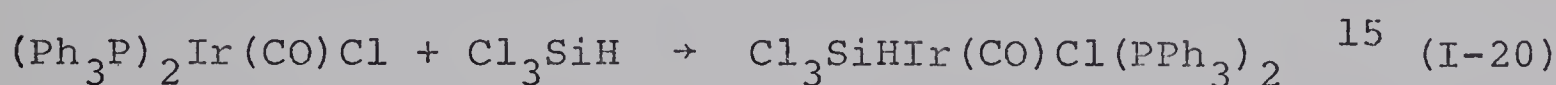
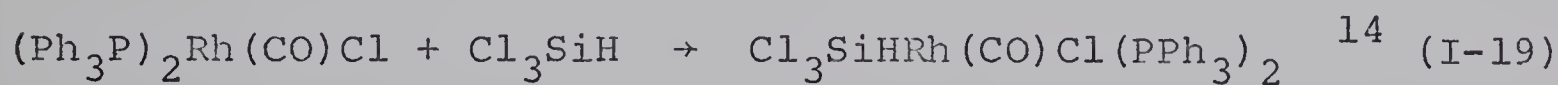
The utilization of the method of (I-16) to synthesize a



series of analogous tin-iron derivatives will be discussed in detail in Chapter VI. Chapter II will discuss some extensions of reactions (I-17) and (I-18) to other silanes and to other metal carbonyls.

#### 4. Oxidative addition reactions.

These reactions refer to the addition of a molecule of a group IV metal to an electronically unsaturated (i.e., short of the effective atomic number of electrons) transition metal complex. The coordination number and the oxidation state of the transition metal is increased by two. As examples:

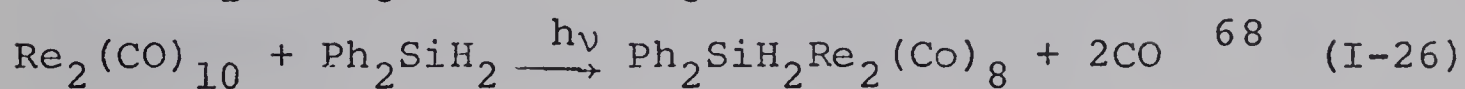
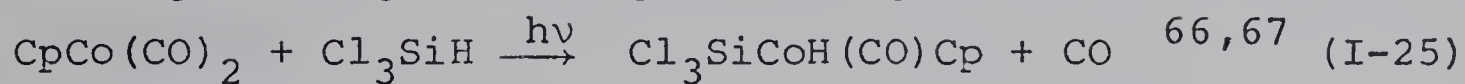
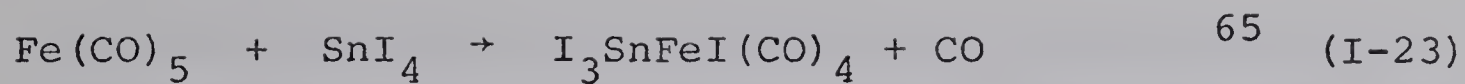


#### 5. Oxidative elimination reactions.

These reactions are similar to the oxidative addition reactions except the group IV molecule is added to a saturated transition metal complex and a ligand such as CO or phosphine is 'eliminated'. Usually the oxidation state of the transition metal is increased by two and coordination number by one for each ligand 'eliminated'. e.g.:







The last three examples of oxidative eliminations (I-24) - (I-26) resemble somewhat the types of reactions to be discussed in Chapters III - V, the major parts of this thesis.





## CHAPTER II

### SILICON-TRANSITION METAL CARBONYL DERIVATIVES FROM THE THERMOLYSES OF POLYFUNCTIONAL SILANES WITH DINUCLEAR METAL CARBONYLS.

#### Introduction

Up to the last 4 or 5 years only a limited number of covalently bonded silicon-transition metal carbonyl derivatives were known. Since most silicon-transition metal carbonyls now known are reasonably stable complexes, it appears that the early dearth was due mainly to the lack of a suitable general synthetic method.

In 1956 Wilkinson and co-workers<sup>11</sup> prepared the first silicon-transition metal complex,  $\text{Me}_3\text{SiFe}(\text{CO})_2\text{Cp}$ , by displacement of the halide ion from  $\text{Me}_3\text{SiCl}$  with the carbonyl anion  $[\text{Fe}(\text{CO})_2\text{Cp}]^-$ . More recently (1965-1968) Aylett and Campbell reported the preparation of  $\text{H}_3\text{SiCo}(\text{CO})_4$ ,<sup>69</sup>  $\text{H}_3\text{SiMn}(\text{CO})_5$ <sup>70</sup> and  $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ <sup>71</sup> by the reaction of the corresponding carbonylate anions with  $\text{H}_3\text{SiI}$ . The halide displacement by carbonyl anions appears to be restricted to strong nucleophiles such as  $[\text{Fe}(\text{CO})_2\text{Cp}]^-$  or unique silicon halides like  $\text{H}_3\text{SiI}$ .

Lappert et al.<sup>9</sup> reported the formation of  $\text{Me}_3\text{SiM}(\text{CO})_3\text{Cp}$  ( $\text{M} = \text{Mo}, \text{W}$ ) from the reaction of  $\text{Me}_3\text{SiNMe}_2$  and  $\text{HM}(\text{CO})_3\text{Cp}$ . The silyl-transition metal carbonyl anions  $[\text{Ph}_3\text{SiFe}(\text{CO})_4]^-$  and  $[\text{Ph}_3\text{SiNi}(\text{CO})_3]^-$ <sup>72</sup> have been synthesized by reacting  $\text{Ph}_3\text{SiLi}$  with  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$ .



The utility of silicon hydrides in synthesizing silicon-transition metal bonds was first demonstrated in 1965 by Chalk and Harrod<sup>13,115,73</sup> when they prepared various tetracarbonylcobalt derivatives  $R_3SiCo(CO)_4$  ( $R = Ph, Cl, OEt, \text{ etc}$ ) from the room temperature reactions of  $R_3SiH$  with  $Co_2(CO)_8$ . By employing more vigorous conditions (up to  $180^\circ$ ) Jetz and Graham<sup>8,10,1</sup> have shown that this was a general route for the synthesis of silicon-transition metal bonds. Compounds in which silicon is bonded to the elements Mn, Re, Cr, Mo, W, Fe, Ni were prepared in this way. Stone et al.<sup>12</sup> prepared  $[Cl_3SiRu(CO)_4]_2$  by the same route.

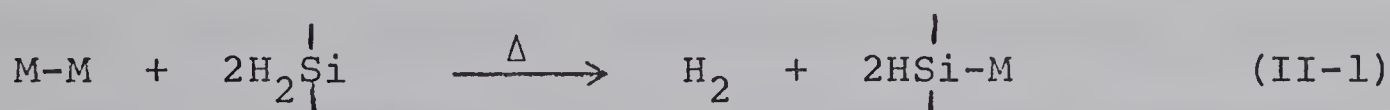
This chapter will describe the extension of these thermal silicon hydride reactions employing polyfunctional silicon hydrides such as  $Me_2SiH_2$  and  $PhSiH_3$ . Reactions of these silanes with transition metal-metal bonded carbonyls afforded a variety of polynuclear silicon-transitional metal carbonyl complexes. Some analogous reactions employing polyfunctional germanium hydrides have also been carried out in this laboratory.<sup>22,75,75</sup> These reactions will be compared to the silicon reactions described here.



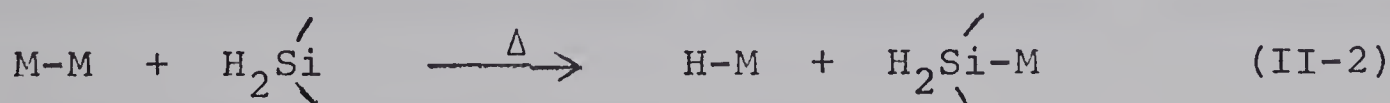
## R E S U L T S   A N D   D I S C U S S I O N

### 1. Synthesis

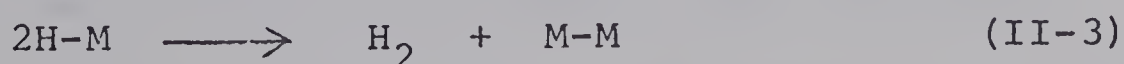
The thermal reactions of polyfunctional silanes with dinuclear transition metal carbonyls initially yielded mononuclear silicon-transition metal carbonyl complexes similar to the compounds obtained with monofunctional silanes. The overall reaction is given in (II-1).



The initial step in these reaction may be the cleavage of the metal-metal bond to give the observed product and the metal hydride:<sup>13</sup>

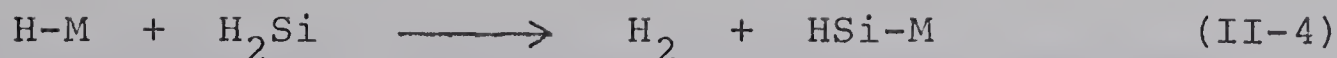


Since the metal hydrides formed in these reactions are unstable at the reaction temperatures employed, decomposition to hydrogen and starting dimer could occur (II-3). Another possibility for the fate of the hydride is reaction with the silane to form more product, with the elimination of hydrogen (II-4). The reaction of  $\text{HMn(CO)}_5$  and  $\text{Me}_3\text{SiH}$  has been shown to yield  $\text{Me}_3\text{SiMn(CO)}_5$  at  $25^\circ$ .<sup>76</sup> Therefore, both pathways seem reasonable and suggests that both could be occurring in these thermal reactions.





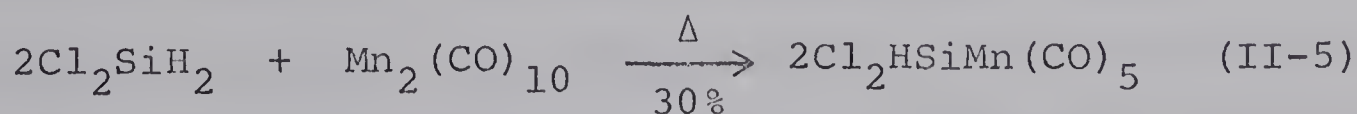




The presence of the second hydrogen in the difunctional silanes  $\text{R}_2\text{SiH}_2$  gives rise to the possibility of further reaction with the metal carbonyl to yield polynuclear species. With this in mind, the thermal reactions of polyfunctional silanes with the metal carbonyls were investigated. The products obtained depended both on the reactants (silane, metal carbonyl) and the reaction conditions (temperature, reaction time, ratio of reactants, etc). In some cases, only mononuclear or only polynuclear species were obtained. The following discussion summarizes the results. All of the reactions were carried out in sealed Carius tubes with excess silane unless otherwise stated (see Experimental for details).

#### Reactions with $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$

The reaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{Ph}_2\text{SiH}_2$  at  $140-150^\circ$  has been shown to yield  $\text{Ph}_2\text{HSiMn}(\text{CO})_5$  and  $[\text{Ph}_2\text{SiMn}(\text{CO})_4]_2$ .<sup>1</sup> The present study has found that dimethylsilane reacted similarly to yield  $\text{Me}_2\text{HSiMn}(\text{CO})_5$  and  $[\text{Me}_2\text{SiMn}(\text{CO})_4]_2$ . Dichlorosilane ( $\text{Cl}_2\text{SiH}_2$ ) reacted at  $130-150^\circ$  to yield only  $\text{Cl}_2\text{HSiMn}(\text{CO})_5$ .

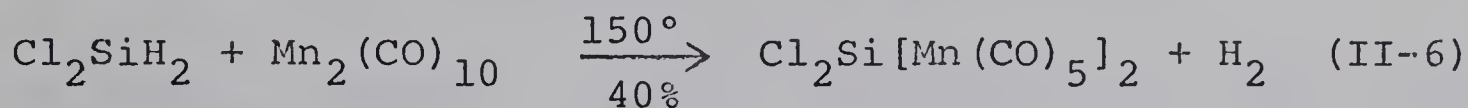


Even at higher temperatures (up to  $200^\circ$ ), which resulted





in much decomposition,  $[\text{Cl}_2\text{SiMn}(\text{CO})_4]_2$  was not obtained. However, when a 1:1 molar ratio of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Cl}_2\text{SiH}_2$  was used, the major product was  $\text{Cl}_2\text{Si}[\text{Mn}(\text{CO})_5]_2$ .



The compound  $\text{Cl}_2\text{Si}[\text{Mn}(\text{CO})_5]_2$  was also obtained by reacting  $\text{Cl}_2\text{HSiMn}(\text{CO})_5$  with  $\text{Mn}_2(\text{CO})_{10}$  at  $150^\circ$ ; this suggested that the mononuclear complex was formed first which then reacted with the excess  $\text{Mn}_2(\text{CO})_{10}$  to form the dinuclear manganese compound.

The complex  $\text{Me}_2\text{HSiMn}(\text{CO})_5$  reacted with bromine at  $0^\circ$  without rupture of the silicon-manganese bond.



Aylett and Campbell<sup>77</sup> have found that  $\text{HCl}$  reacted similarly with  $\text{H}_3\text{SiMn}(\text{CO})_5$ .

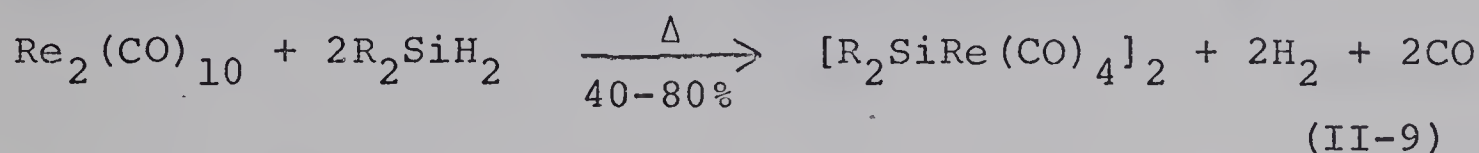


With the exception of  $\text{Me}_2\text{HSiMn}(\text{CO})_5$ , which was an air-sensitive liquid, all the manganese-silicon compounds prepared were moderately air-stable crystalline solids.

Rhenium carbonyl ( $\text{Re}_2(\text{CO})_{10}$ ) reacted with difunctional silanes in a similar manner to manganese carbonyl, but there were some differences. Thus, dichlorosilane reacted at  $150$ - $195^\circ$  to yield  $\text{Cl}_2\text{HSiRe}(\text{CO})_5$  and  $[\text{Cl}_2\text{SiRe}(\text{CO})_4]_2$  with



the latter in very low yield (ca. 5% at most); in contrast, the analogous manganese dimer could not be obtained as noted above. However, the organosilanes  $R_2SiH_2$  ( $R = Me, Et, Ph$ ) gave only  $[R_2SiRe(CO)_4]_2$  in good yields.



For example, diphenylsilane and rhenium carbonyl did not react at all at  $140^\circ$ ; while at  $160^\circ$  a 70% yield of  $[Ph_2SiRe(CO)_4]_2$  was obtained. Work by E. H. Brooks in this laboratory established that diorganogermanes  $R_2GeH_2$  reacted with either  $Mn_2(CO)_{10}$  or  $Re(CO)_{10}$  to yield only the  $[R_2GeM(CO)_4]_2$  dimers, no matter what the ratio of reactants.<sup>75</sup> This indicates a higher reactivity of the second Ge-H bond relative to the second Si-H bond in thermal reactions with metal carbonyls. This aspect is discussed further in connection with the reactions of cobalt carbonyl.

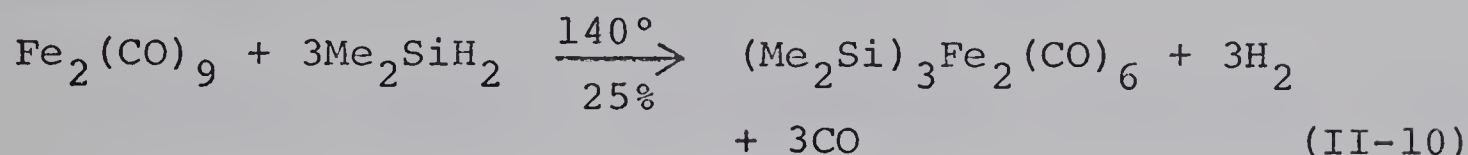
#### Reactions with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$

The binary carbonyls of iron,  $Fe_2(CO)_9$  and  $Fe_3(CO)_{12}$  reacted with dichlorosilane at  $70-80^\circ$  to yield  $[Cl_2SiFe(CO)_4]_2$  as the only isolable compound. This compound has previously been prepared at higher temperatures ( $160-180^\circ$ ) from  $Cl_3SiH$  and  $Fe_3(CO)_{12}$ .<sup>8</sup> Higher temperatures were required in the latter case, probably because a silicon-



chlorine bond must be broken during the reaction.

With dimethylsilane,  $\text{Fe}_2(\text{CO})_9$  reacted to form  $(\text{Me}_2\text{Si})_3\text{Fe}_2(\text{CO})_6$ .



Spectral evidence (infrared, mass) for other species such as  $\text{R}_2\text{SiFe}_2(\text{CO})_8$  and  $(\text{R}_2\text{Si})_2\text{Fe}_2(\text{CO})_8$  were obtained but because of the instability of the complexes and the intractable nature of the reaction mixtures, complete characterization could not be made. With germanes,  $\text{R}_2\text{GeH}_2$ , the products of analogous reactions are more stable, and numerous complexes have been obtained. For example  $\text{R}_2\text{GeFe}_2(\text{CO})_8$ <sup>22</sup>,  $[\text{R}_2\text{GeFe}(\text{CO})_4]_2$ <sup>22</sup>,  $(\text{R}_2\text{Ge})_2\text{Fe}_2(\text{CO})_7$ <sup>78</sup>,  $(\text{R}_2\text{Ge})_3\text{Fe}_2(\text{CO})_6$ <sup>22,79</sup> and  $(\text{R}_2\text{Ge})_2\text{Fe}_3(\text{CO})_9$ <sup>80</sup> have all been isolated and characterized.

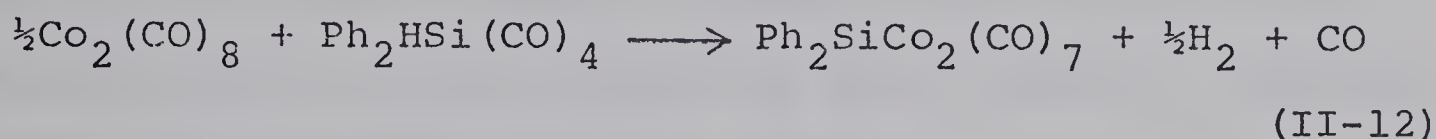
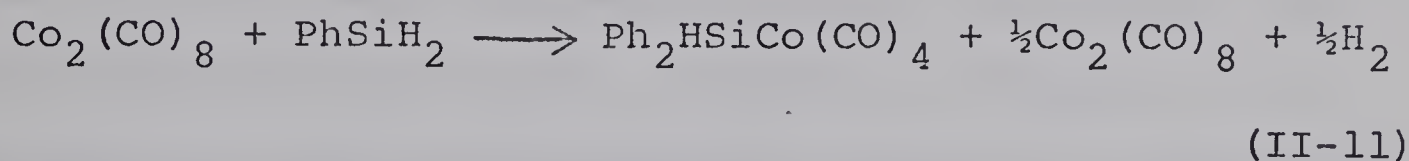
#### Reactions with $\text{Co}_2(\text{CO})_8$

Cobalt carbonyl reacted with silanes at room temperature as reported by Chalk and Harrod.<sup>13</sup> However, the silylcobalt derivatives were much more thermally and oxidatively unstable than derivatives of the other metals. With excess diphenylsilane, cobalt carbonyl reacted to form  $\text{Ph}_2\text{HSiCo}(\text{CO})_4$  as previously reported.<sup>73</sup> In the present work, using a 1:1 molar ratio of  $\text{Co}_2(\text{CO})_8$  and



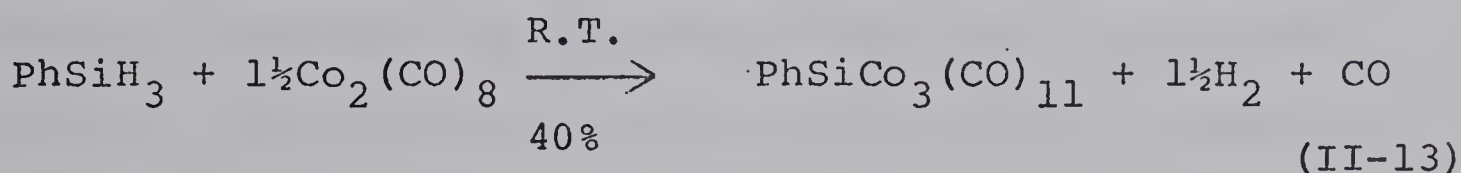


$\text{Ph}_2\text{SiH}_2$ , the compound  $\text{Ph}_2\text{HSiCo(CO)}_4$  was first formed and then reacted slowly with the excess  $\text{Co}_2(\text{CO})_8$  to afford the air-sensitive, yellow, crystalline  $\text{Ph}_2\text{SiCo}_2(\text{CO})_7$  (infrared monitoring).



Recent studies on the reaction of  $\text{Ph}_2\text{GeH}_2$  with  $\text{Co(CO)}_8$  have found that  $\text{Ph}_2\text{GeCo}_2(\text{CO})_7$  was the only product regardless of the stoichiometries of the reactants.<sup>74,81</sup>

Phenylsilane ( $\text{PhSiH}_3$ ) reacted with cobalt carbonyl (using exact molar ratios) in a stepwise sequence to form the undecacarbonyl.



Attempts to convert this compound to the nonacarbonyl  $\text{PhSiCo}_3(\text{CO})_9$  have led only to decomposition. Noncarbonyl-tricobalt silicon derivatives have been reported by Kettle and Khan<sup>82,83</sup> but attempts in this laboratory to repeat their syntheses have been unsuccessful. The carbon analogs  $\text{RCCo}_3(\text{CO})_9$  are, however, very stable, well characterized compounds.<sup>84,85</sup> The germanium derivative





$\text{PhGeCo}_3(\text{CO})_{11}$  has recently been prepared in this laboratory and has been successfully converted to the nonacarbonyl  $\text{PhGeCo}_3(\text{CO})_9$ .<sup>86</sup>

The foregoing discussion gives an indication of the types of silyl-transition metal carbonyl derivatives that can be obtained from thermal reactions. It appears that more extensive work on the thermal reactions of other polyfunctional silanes and metal carbonyls will afford other new polynuclear silicon-transition metal carbonyl complexes.

The compounds described in this Chapter were characterized by elemental analyses, mass spectra, infrared and nmr spectra. Results were consistent with the postulated formulations (see Experimental section for tabulated results). The mass spectra of the complexes all showed the molecular ion and the stepwise loss of the appropriate number of carbonyls. Mass spectra of transition metal carbonyl compounds are discussed more fully in the next Chapter. The infrared spectra in the carbonyl region are now discussed in relation to the structures.

## 2. Infrared Spectra and Structure

The carbonyl stretching region of the infrared spectrum is a valuable aid in the study of transition metal carbonyl complexes. Besides the standard empirical uses such as following reactions or testing for impurities, the carbonyl stretching bands can be used to infer structures and the



general chemical nature of the complexes. Qualitatively the relative band intensities, band frequencies, and overall band patterns can be compared to the spectra of compounds of known structure. The symmetries of the molecules can be used to predict the number of carbonyl stretching bands expected for a given structure.

Most carbonyl stretching bands for electrically neutral complexes occur in the region  $1750\text{--}2150\text{ cm}^{-1}$ . Carbon monoxide itself absorbs at  $2143\text{ cm}^{-1}$ . Terminal carbonyls absorb in the region  $1900\text{--}2150\text{ cm}^{-1}$  while bridging carbonyls absorb in the lower  $1750\text{--}1900\text{ cm}^{-1}$  region. The carbonyl bands in cationic and anionic complexes are shifted (ca.  $50\text{--}150\text{ cm}^{-1}$ ) to higher and lower energies respectively. Other ligands bonded to the transition metal such as phosphines, which are poorer  $\pi$ -acceptors than CO, will shift the carbonyl stretching bands to lower frequencies than in the pure binary carbonyls.

By the use of group theory the number of infrared and Raman active carbonyl stretching frequencies can be predicted for a given structure. The overall symmetry of the molecule is used when determining the number of infrared active carbonyl stretching vibrations.

It has been found that hydrocarbon solvents such as pentane, hexane or cyclohexane give very strong and sharp carbonyl bands with concentrations of  $10^{-3} - 10^{-4}$  molar.

88,89 Bands separated by as little as  $3 - 4\text{ cm}^{-1}$  can

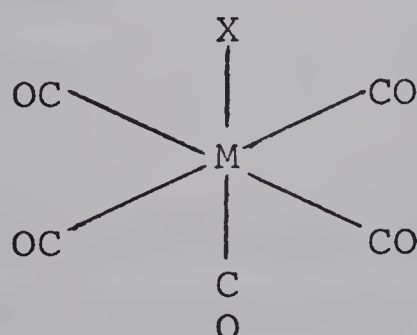


usually be resolved on modern grating instruments. Almost all spectra given in this work were taken with cyclohexane as solvent.

The following discussion of the structures and spectroscopic properties of the compounds reported in this Chapter will serve to illustrate the value of the carbonyl stretching region of the infrared spectrum.

### Pentacarbonyl Manganese and Rhenium Derivatives.

The silicon derivatives of manganese and rhenium pentacarbonyl show three main CO stretching frequencies as expected for idealized  $C_{4v}$  symmetry, 11 (as shown in Figure 1). If the group attached to the  $M(CO)_5$  moiety is unsymmetrical, more bands are usually observed (Figures 2 and 3). In Figure 3 the broad band at ca.  $2143\text{ cm}^{-1}$  is due to the Si-H stretch. Infrared studies of various tin, germanium and silicon derivatives of manganese and rhenium pentacarbonyl have been carried out by a number of groups <sup>87,90,10</sup> and the interpretation of spectra is well established.







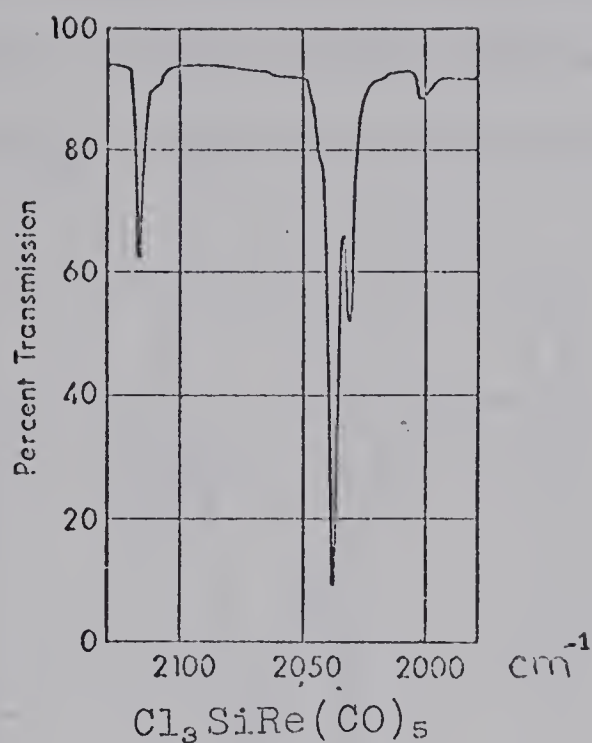


FIGURE 1

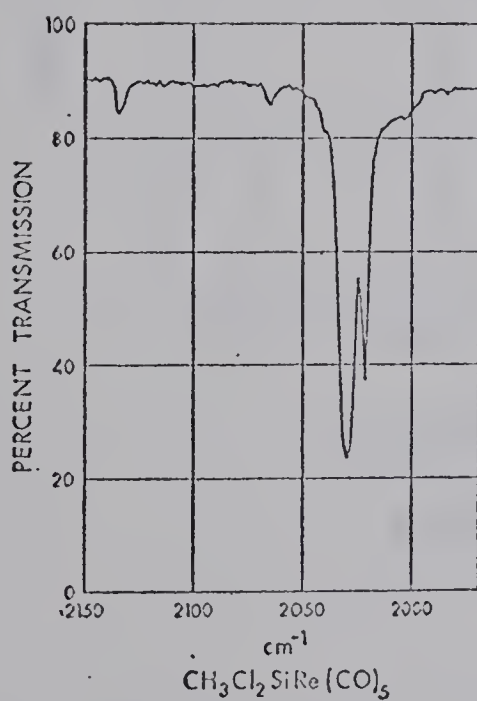


FIGURE 2

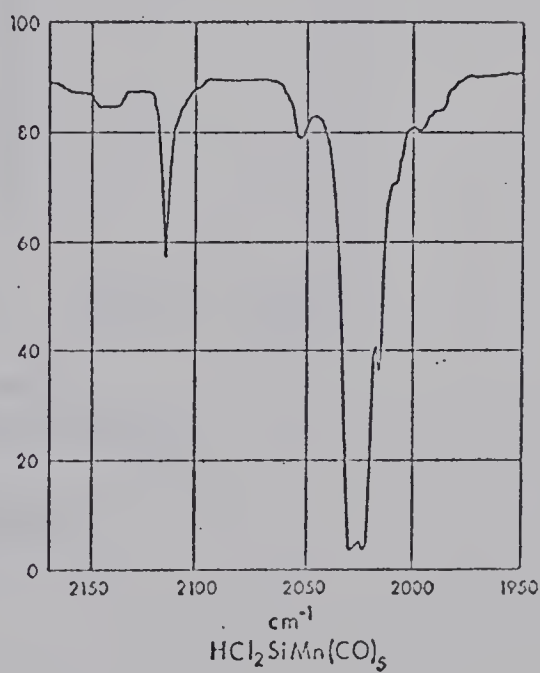


FIGURE 3

The compound  $\text{Cl}_2\text{Si}[\text{Mn}(\text{CO})_5]_2$  shows six carbonyl bands (Figure 4); a maximum of eight bands is expected for the  $\text{C}_{2v}$  configuration as found in the X-ray structure determination of the presumably isostructural  $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ .<sup>43</sup>





It is interesting to note that the band pattern in Figure 4 is almost identical to that of the analogous tin compound,  $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ , reported by Thompson and Graham.<sup>26</sup>

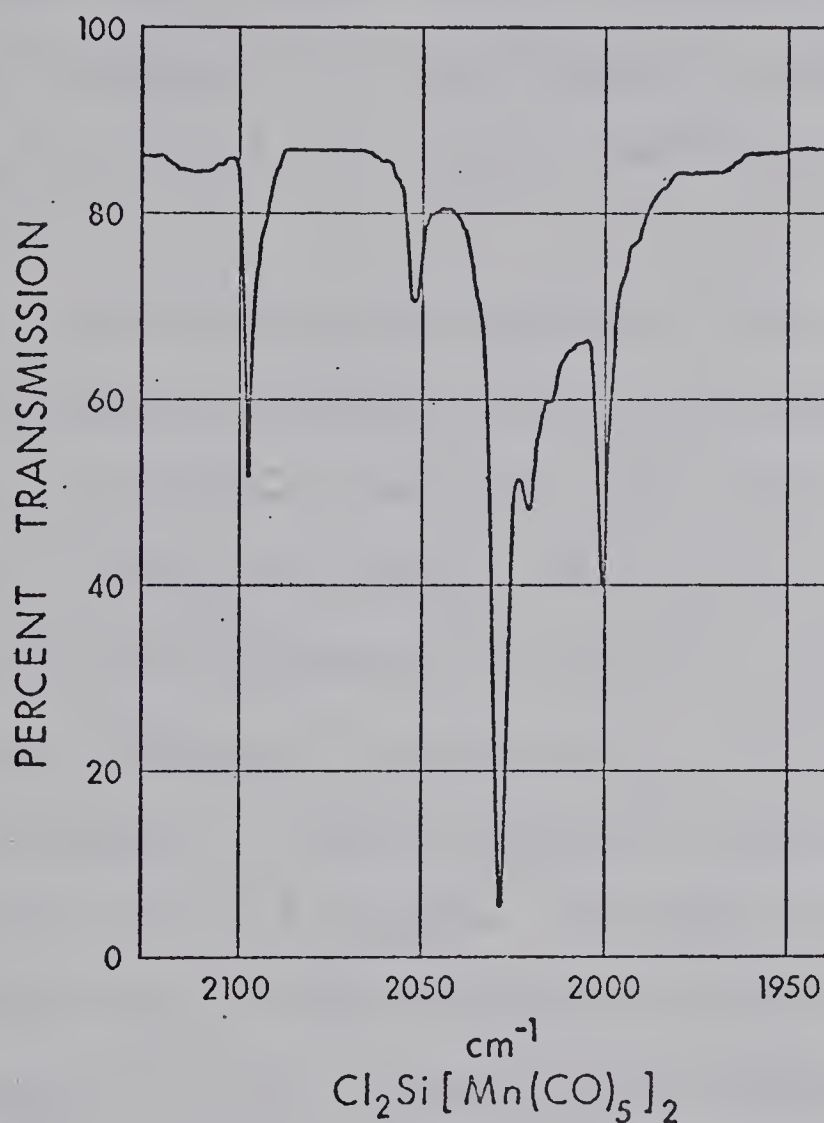


FIGURE 4

Complexes  $[\text{R}_2\text{SiM}(\text{CO})_4]_2$   $\left( \begin{array}{l} \text{M} = \text{Mn} ; \text{ R} = \text{Me} \\ \text{M} = \text{Re} ; \text{ R} = \text{Me, Et, Ph, Cl} \end{array} \right)$

The infrared spectra of these complexes show three or four carbonyl stretching bands (Figures 5-8); for the proposed  $\text{D}_{2h}$  structure as found in the tetracarbonyl halide dimers of manganese and rhenium,<sup>37</sup> four bands



( $B_{1u} + B_{2u} + 2B_{3u}$ ) are predicted. The compounds which show only three bands ( $[\text{Et}_2\text{SiRe}(\text{CO})_4]_2$  and  $[\text{Me}_2\text{SiRe}(\text{CO})_4]_2$ ) have one carbonyl band (lowest energy one) which is much broader than the others; this is probably due to the accidental degeneracy of two bands. In fact for the complex  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$  the fourth band appears as a shoulder (Figure 5).

X-ray crystallographic studies have shown that these silyl compounds do possess the  $D_{2h}$  structure similar to that that found by Dahl and Wei for  $[\text{BrMn}(\text{CO})_4]_2$ .<sup>38</sup> The crystal structure of  $[\text{Ph}_2\text{SiMn}(\text{CO})_4]_2$  (prepared by W. Jetz in this laboratory) was determined by Dahl.<sup>39</sup> The structure of the rhenium compound  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$  was determined by Haas and Bennett<sup>91</sup> and is shown in Figure 9 with selected bond angles and bond lengths. The EAN rule predicts a metal-metal bond in these silyl derivatives and no bond (metal-metal) for the tetracarbonyl halide dimers. The bond lengths as determined from X-ray crystallography are consistent with this; Mn-Mn distances for  $\text{Mn}_2(\text{CO})_{10}$ ,  $[\text{Ph}_2\text{SiMn}(\text{CO})_4]_2$  and  $[\text{BrMn}(\text{CO})_4]_2$  are  $2.92 \text{ \AA}$ <sup>40</sup>,  $2.87 \text{ \AA}$ <sup>39</sup>,  $3.74 \text{ \AA}$ <sup>38</sup> respectively while Re-Re distances are  $3.02 \text{ \AA}$ <sup>40</sup> and  $3.00 \text{ \AA}$ <sup>91</sup> for  $\text{Re}_2(\text{CO})_{10}$  and  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$ . The acute Re-Si-Re angle of  $76^\circ$  in  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$  lends further support to a metal-metal interaction.



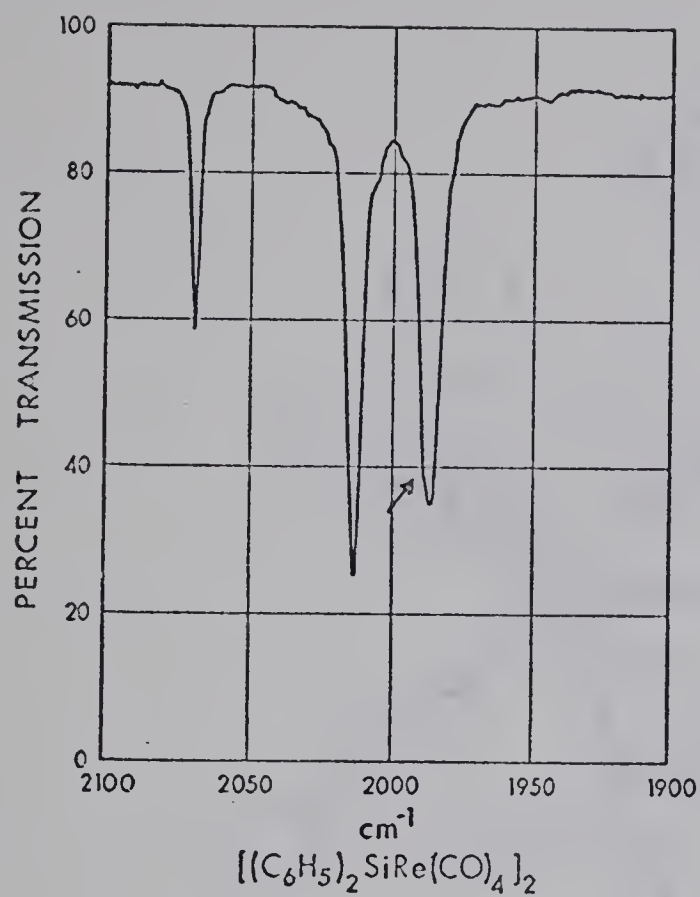


FIGURE 5

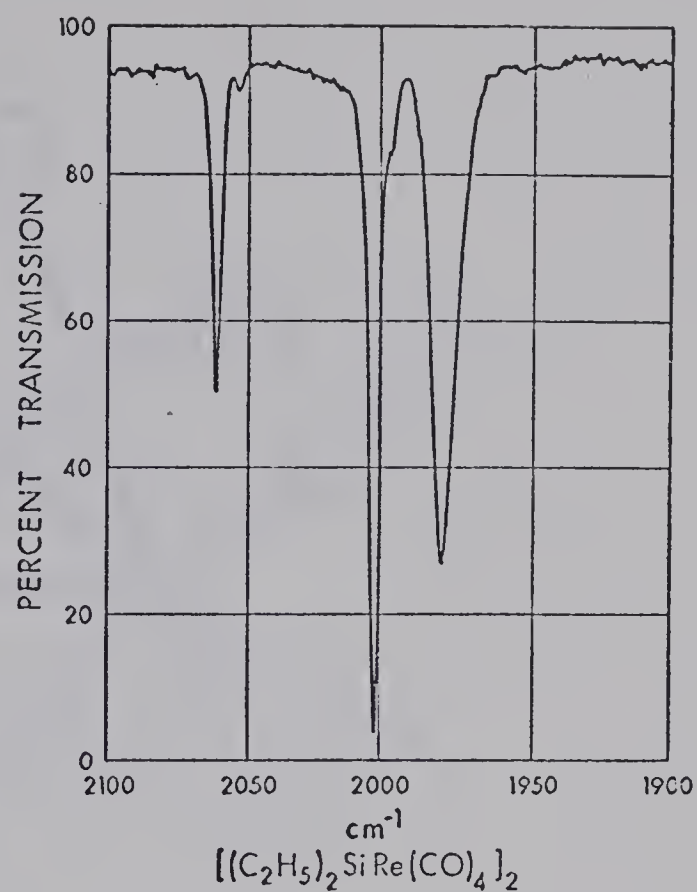


FIGURE 6

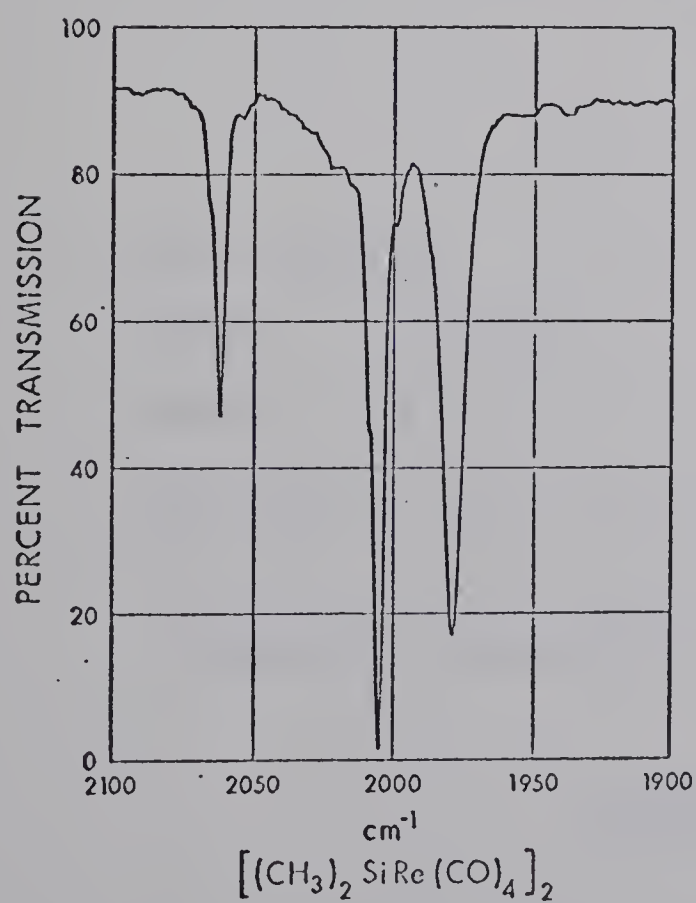


FIGURE 7

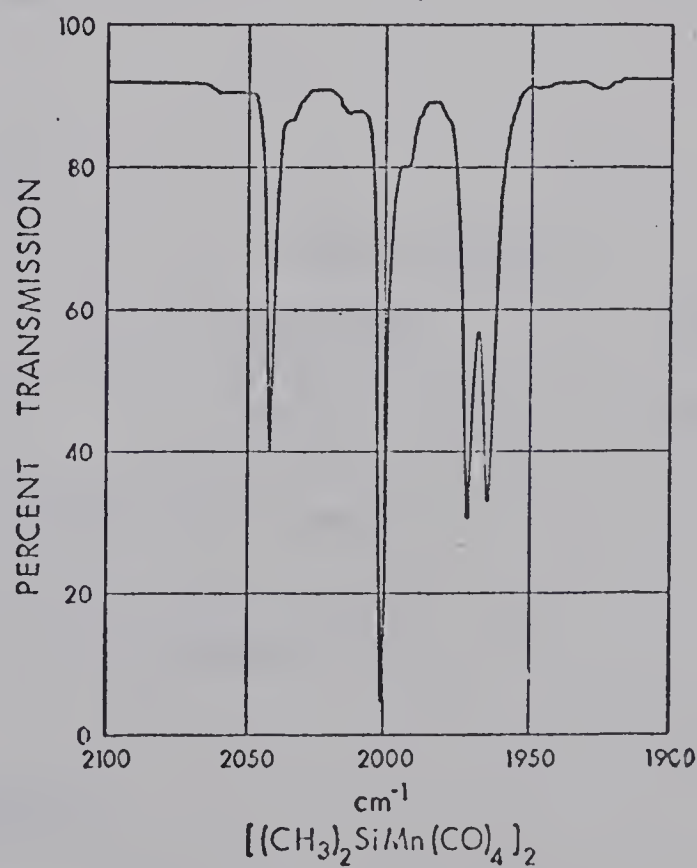
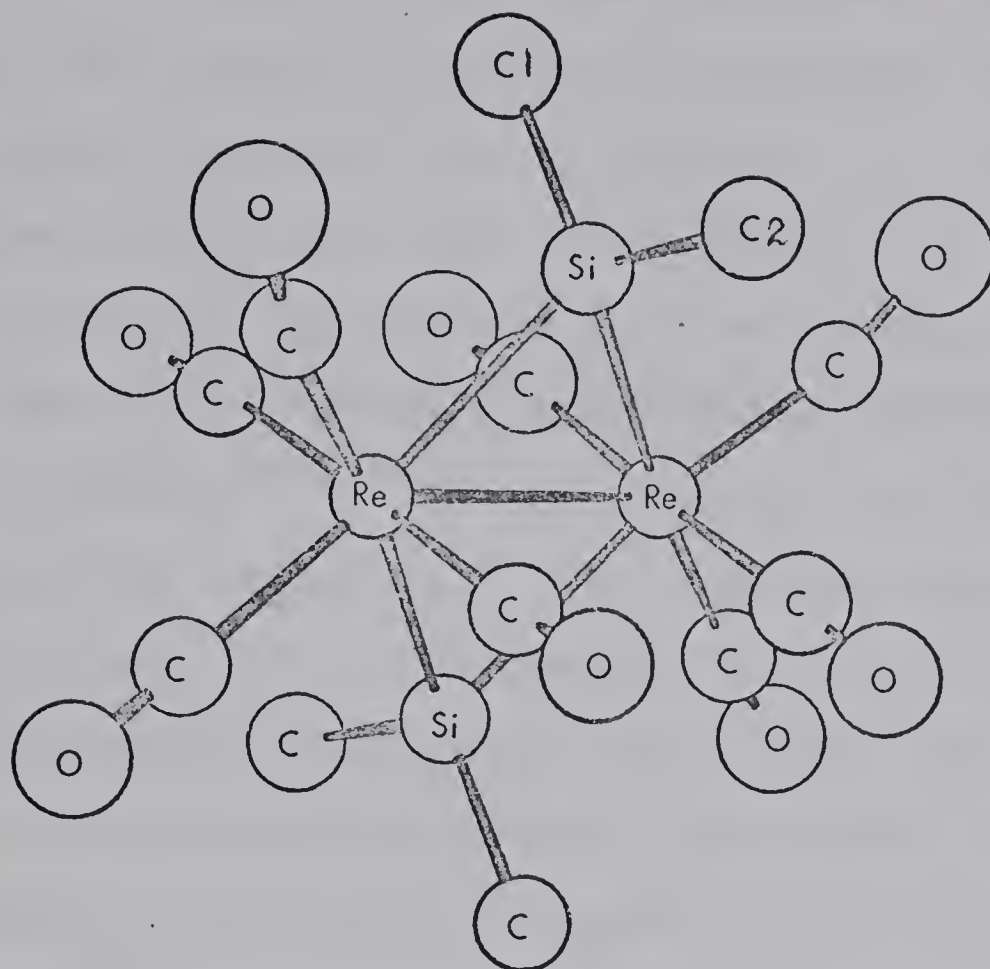


FIGURE 8





Bond lengths

Re-Re      3.00 Å

Re-Si      2.52 Å

Bond angles

Re-Si-Re      75°

C(1)-Si-C(2)      109°

The phenyl rings are omitted for clarity

MOLECULAR STRUCTURE OF  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$ <sup>91</sup>

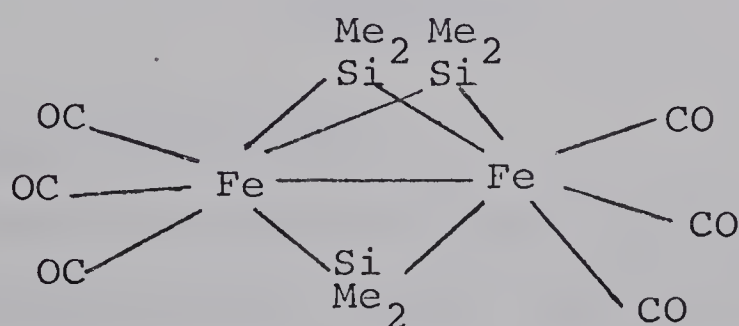
FIGURE 9





### The Complex $(\text{Me}_2\text{Si})_3\text{Fe}_2(\text{CO})_6$

Figure 10 shows the infrared spectrum of  $(\text{Me}_2\text{Si})_3\text{Fe}_2(\text{CO})_6$ ; the two carbonyl stretching frequencies observed are the number predicted for  $D_{3h}$  symmetry, 12. This structure can be derived from that of  $\text{Fe}_2(\text{CO})_9$ , 9 by replacing the three bridging carbonyls with three bridging  $\text{Me}_2\text{Si}$  groups. The X-ray structure determination of the analogous germanium compound <sup>22,79</sup>  $(\text{Me}_2\text{Ge})_3\text{Fe}_2(\text{CO})_6$  has shown that the structure is indeed  $D_{3h}$ . The germanium compound has an Fe-Fe distance of 2.76 Å compared to 2.46 Å in  $\text{Fe}_2(\text{CO})_9$ .<sup>51</sup> If the differences in the Fe-Fe bond lengths are related to the Fe-Ge and Fe-C distances in the bridges, the iron-iron distance in the silicon compound should be intermediate between the two.





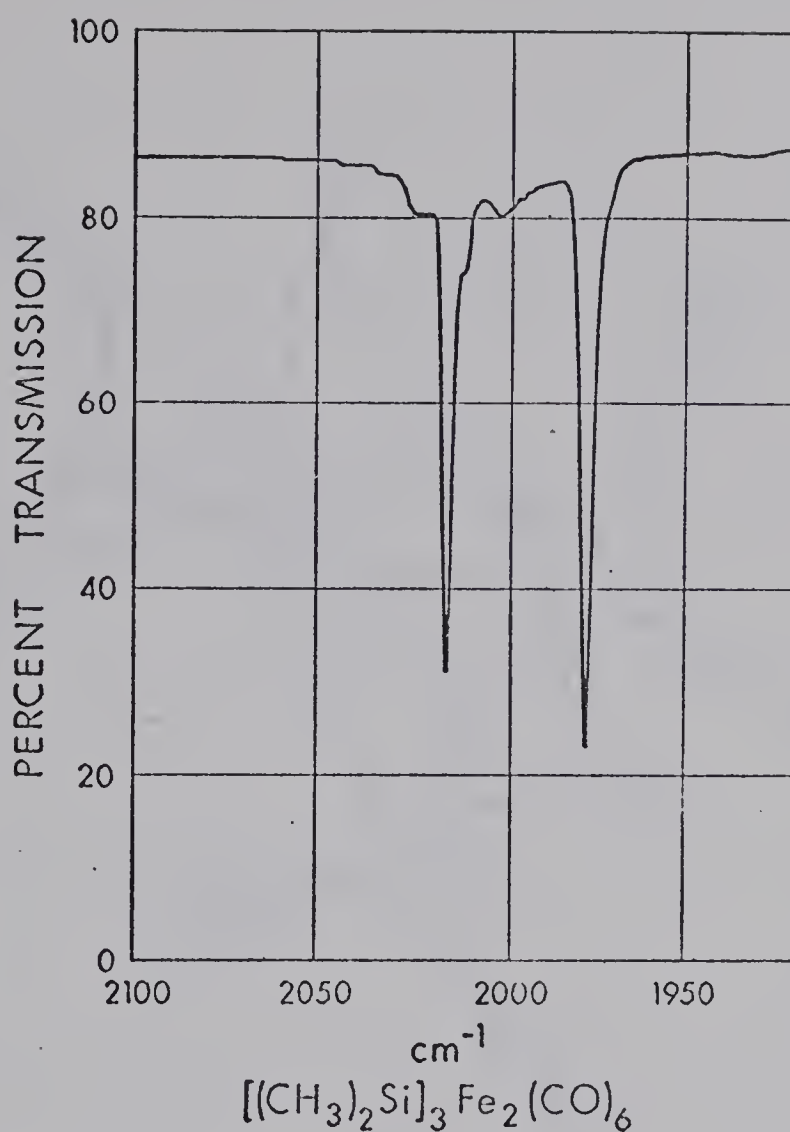
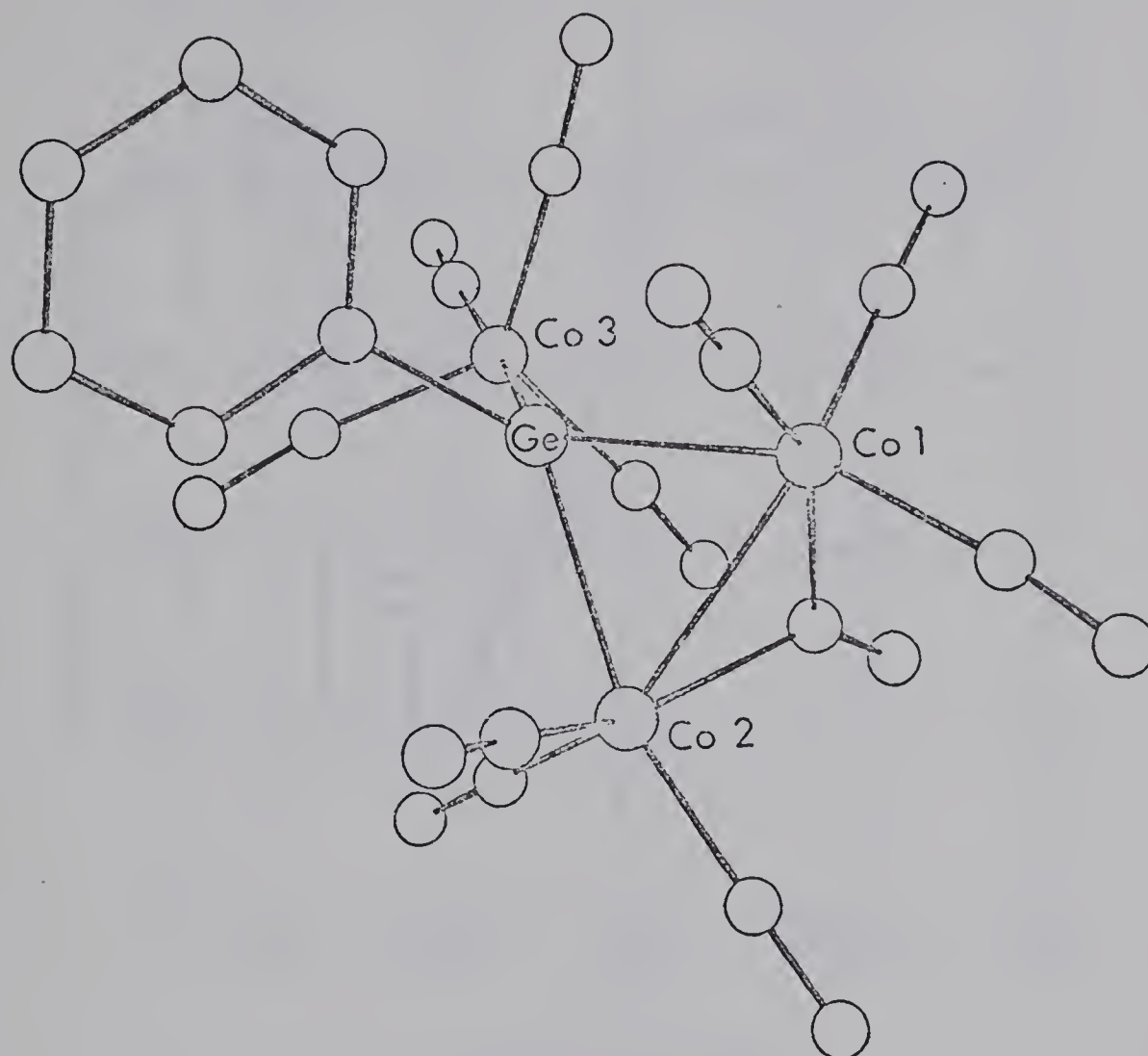


FIGURE 10

### Silicon-Cobalt Derivatives.

The cobalt derivatives  $Ph_2SiCo_2(CO)_7$  and  $PhSiCo_3(CO)_{11}$  exhibit infrared spectra almost identical to the germanium analogs <sup>74,81,86</sup> and undoubtedly the structures are the same. The structure of  $PhGeCo_3(CO)_{11}$  has been determined <sup>86</sup> and is shown in Figure 11; this structure can be obtained by replacing one of the bridging carbonyls in  $Co_2(CO)_8$ , <sup>8</sup> with a  $PhGeCo(CO)_4$  group. The most probable structure for  $Ph_2SiCo_2(CO)_7$  as suggested by the infrared spectrum is the one shown in 13.





MOLECULAR STRUCTURE OF  $\text{PhGe}_3(\text{CO})_{11}$  <sup>86</sup>

FIGURE 11



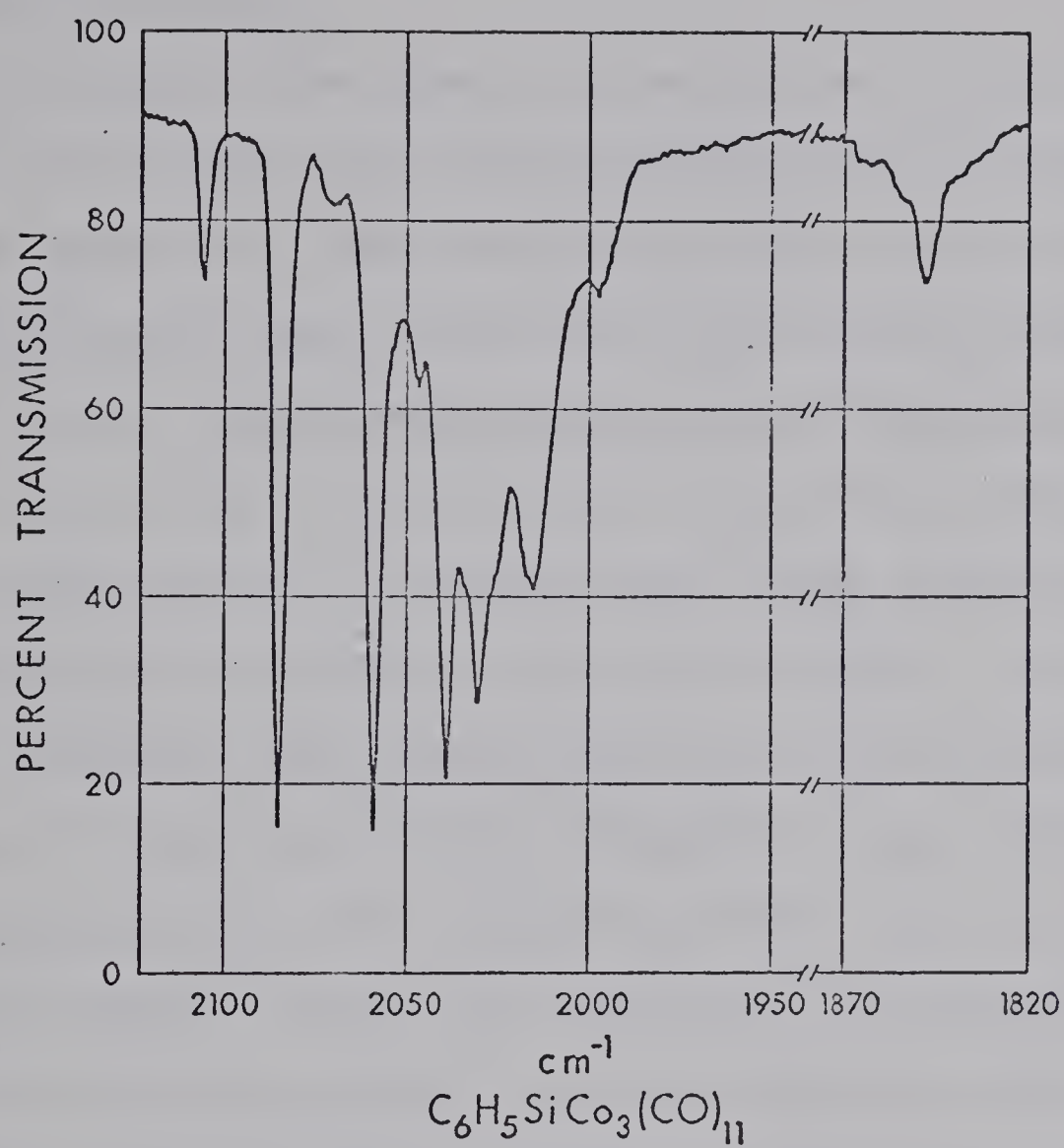
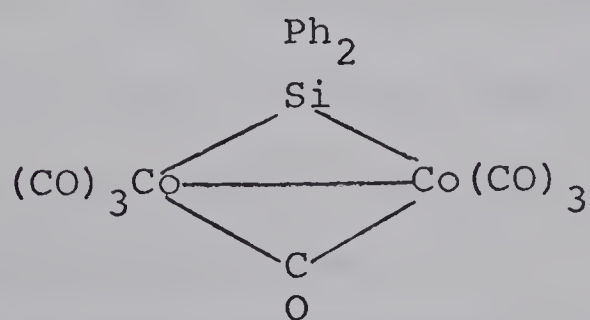


FIGURE 12







## E X P E R I M E N T A L

### General Techniques.

A nitrogen atmosphere was maintained during all reactions and during work up procedures mainly by the use of Schlenk apparatus. The majority of the silane reactions in this Chapter were carried out using Carius tubes of ca. 70 ml volume. These were constructed of thick-walled Pyrex tubing with a thick-walled constricted section for facile sealing and a standard taper 14/20 joint at one end for convenient attachment to a vacuum system. Solid and liquid reagents were placed directly into the tube. Weighed amounts of the more volatile compounds (e.g.,  $\text{Cl}_2\text{SiH}_2$  b.p. =  $8^\circ$ ;  $\text{Me}_2\text{SiH}_2$  b.p. =  $-20^\circ$ ) were distilled into the tube using a vacuum system. After all components were placed in the tube, the tube was cooled in liquid nitrogen and sealed off under vacuum. The reaction was carried out by completely immersing the sealed tube into a thermostated silicone oil bath. After reaction the tubes were cooled in liquid nitrogen, opened, and the volatiles were pumped off. Procedures from this point varied for each reaction and are given in the preparations below.

Melting points were taken using a microscope equipped with a Kofler hot stage. Microanalyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany and by the micro-



analytical laboratory of this department. Results are given in Table III.

### Spectroscopy

Mass spectra were obtained on Associated Electrical Industries MS-9 or MS-12 spectrometers. Nmr spectra were recorded using Varian A-60 and HA-100 spectrometers with TMS as internal standard; results are summarized in Table IV.

Infrared spectra in the carbonyl stretching region were measured using a Perkin-Elmer model 337 spectrometer equipped with expanded scale readout accessory and a Hewlett Packard Model 7127A recorder. The expanded spectrum obtained on the recorder ( $100\text{ cm}^{-1} = 13\text{ cm}$  of chart paper) was calibrated above and below the region of interest by introducing gas cells containing carbon monoxide or deuterium bromide into the sample beam at the appropriate times during a continuous run. Samples were then measured by interpolation using CO band number 31 and DBr band number 13.<sup>92</sup> The linearity of the wave-number scale in this interval was established using gaseous deuterium chloride. Deviations between duplicate spectra did not exceed  $1\text{ cm}^{-1}$  and the accuracy of the figures is well within the limits  $\pm 1\text{ cm}^{-1}$ . All spectra were obtained in cyclohexane solution using 0.5 mm thickness KBr cells and concentrations of 0.5 to 1.0 mg/ml.



Carbonyl stretching frequencies are given in Table IV.

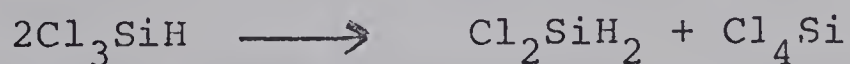
### Materials

Silanes ( $\text{Cl}_3\text{SiH}$ ,  $\text{Me}_2\text{SiH}_2$ ,  $\text{Et}_2\text{SiH}_2$ ,  $\text{Ph}_2\text{SiH}_2$ ,  $\text{PhSiH}_3$ ) were purchased from Pierce Chemical Company, Rockford, Illinois and were used as supplied. Samples of  $\text{Co}_2(\text{CO})_8$  and  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  were purchased from Strem Chemicals Inc., Danvers, Mass. and were sublimed or recrystallized before use. The carbonyls  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$  were obtained from Alfa Inorganics Inc., Beverly, Mass. The compounds  $\text{Re}_2(\text{CO})_{10}$  and  $\text{Mn}_2(\text{CO})_{10}$  were purchased from Pressure Chemical Co., Pittsburgh, Pa. Solvents were of reagent grade and were dried over sodium wire or calcium hydride and saturated with dry nitrogen prior to use.

### Procedures

#### Dichlorosilane, $\text{Cl}_2\text{SiH}_2$

Samples of this compound were prepared by the catalytic disproportionation of trichlorosilane according to a patented procedure.<sup>93</sup>



A representative procedure for preparing  $\text{Cl}_2\text{SiH}_2$  is as follows. Dropwise addition of 7.0 ml 4-methylpyridine to a one litre 3-neck flask containing 300 ml trichlorosilane and 300 ml sym-tetrachloroethane resulted in the





formation of a small amount of white solid. The flask was connected to a vacuum-jacketed column (1 meter long; i.d. = 1.5 cm packed with glass helices) equipped with a  $-78^{\circ}$  cooled still head and receiver. The mixture was refluxed for six hours (oil bath temperature  $55-60^{\circ}$ ). Then the still head was warmed to  $0^{\circ}$  and maintained at  $0-4^{\circ}$  during collection of the product; pot temperature was maintained at  $55^{\circ}$  during distillation. A total of 25 ml of distillate was obtained. The nmr spectrum showed that the product was ca. 95% pure.

Dichlorosilylpentacarbonylmanganese,  $\text{Cl}_2\text{HSiMn}(\text{CO})_5$ .

A Carius tube containing manganese carbonyl (2.71 g, 6.9 mmol) and 30 g dichlorosilane was heated at  $155-160^{\circ}$  for 24 hours. Removal of excess dichlorosilane and room temperature sublimation (0.01 mm without continuous pumping) afforded 1.25 g (30%) of white crystalline product.

Dimethylsilylpentacarbonylmanganese,  $\text{Me}_2\text{HSiMn}(\text{CO})_5$ .

Heating a sealed Carius tube containing 2.09 g (5.4 mmol)  $\text{Mn}_2(\text{CO})_{10}$  and 2.0 g (33 mmol)  $\text{MeSiH}_2$  for three hours at  $150^{\circ}$  gave a dark-red solution. Removal of excess dimethylsilane at reduced pressure and vacuum distillation of the residue (room temperature 0.01mm) into a  $-78^{\circ}$  trap gave 2.0 g (73%) of  $\text{Me}_2\text{HSiMn}(\text{CO})_5$  as a pale-yellow, air-sensitive liquid.





(Dimethylbromosilyl)pentacarbonylmanganese,  $\text{Me}_2\text{BrSiMn}(\text{CO})_5$

A solution of  $\text{Me}_2\text{HSiMn}(\text{CO})_5$  (1.0 g) and bromine (0.75 g) in 50 ml cyclohexane was stirred at  $0^\circ$  for two hours. Solvent and excess bromine were removed at reduced pressure. Residual solid was crystallized from hexane to afford a pale-yellow solid which on sublimation at room temperature gave white crystals of the product (0.60 g; 45%).

Dichlorobis(pentacarbonylmanganese)silicon(IV),

$\text{Cl}_2\text{Si}[\text{Mn}(\text{CO})_5]_2$

A sealed Carius tube containing a solution of  $\text{Mn}_2(\text{CO})_{10}$  (0.53 g, 1.4 mmol) and  $\text{Cl}_2\text{HSiMn}(\text{CO})_5$  (0.80 g, 2.8 mmol) in 2 ml n-hexane was heated for ten hours at  $150^\circ$ . Removal of n-hexane at reduced pressure and sublimation at  $30^\circ$  (0.01 mm) removed unreacted starting materials. Crystallization of the unsublimed solid from n-hexane yielded pale-yellow crystals of  $\text{Cl}_2\text{Si}[\text{Mn}(\text{CO})_5]_2$  (0.30 g, 43%).

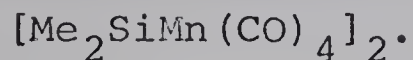
Trans-diphenylsilyl(tetracarbonyl)(triphenylphosphine)-  
manganese,  $\text{trans-Ph}_2\text{HSiMn}(\text{CO})_4\text{PPh}_3$ .

Diphenylsilane (0.60 g, 3.26 mmol) and  $[\text{Ph}_3\text{PMn}(\text{CO})_4]_2$  (1.31 g, 1.53 mmol) were heated at  $145^\circ$  in a sealed Carius tube with 2 ml cyclohexane for 20 hours. Removal



of solvent at reduced pressure and two recrystallizations of the residue from dichloromethane-hexane afforded white crystals (1.37 g, 73%) of the product.

Di-μ-dimethylsilicon-bis(tetracarbonylmanganese),



A Carius tube containing 2.65 g (6.80 mmol)  $\text{Mn}_2(\text{CO})_{10}$  and 3.1 g (52 mmol) dimethylsilane was heated for five hours at 185°. After removal of excess dimethylsilane, the  $\text{Me}_2\text{HSiMn}(\text{CO})_5$  (1.0 g) was distilled under high vacuum into a -78° trap. The remaining solid was recrystallized twice from n-hexane and sublimed once to afford 0.30 g (10%) of pale-yellow crystalline product.

Di-μ-dimethylsilicon-bis(tetracarbonylrhenium),



Heating 2.0 g (3.1 mmol)  $\text{Re}_2(\text{CO})_{10}$  and 2.3 g (38 mmol) dimethylsilane for 44 hours (160°) in a sealed Carius tube gave a dark-red reaction mixture. After removal of volatiles at reduced pressure, the residual solid was recrystallized twice from n-hexane to yield buff-coloured crystals of  $[\text{Me}_2\text{SiRe}(\text{CO})_4]_2$  (0.30 g, 14%).

Di-μ-diethylsilicon-bis(tetracarbonylrhenium),



Rhenium carbonyl (1.13 g, 1.73 mmol) and diethylsilane (1.5 g, 17 mmol) were heated in a Carius tube



at 155° for 19 hours. Volatiles were removed at reduced pressure and the remaining solid was sublimed (55°/0.01mm) for 6 hours to remove most of the  $\text{Re}_2(\text{CO})_{10}$ . Two recrystallizations from n-hexane afforded 0.25 g (29%) of pale-yellow crystals.

Di- $\mu$ -diphenylsilicon-bis(tetracarbonylrhenium),  
 $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$

A Carius tube with 2.0 g (3.07 mmol)  $\text{Re}_2(\text{CO})_{10}$  and 2.0 g (10.9 mmol) diphenylsilane was heated for 120 hours at 165°. At the start of the reaction the tube contained a colorless solution but as the reaction proceeded large crystals of the product were deposited. After removing volatiles at reduced pressure, the crystals were washed with n-hexane (two 15 ml portions) and dried under high vacuum to yield 1.26 g (38%) of pale-yellow crystals.

Dichlorosilylpentacarbonylrhenium and Di- $\mu$ -dichlorosili-  
con-bis(tetracarbonylrhenium),  $\text{Cl}_2\text{HSiRe}(\text{CO})_5$  and  
 $[\text{Cl}_2\text{SiRe}(\text{CO})_4]_2$ .

Dichlorosilane (3.0 g, 29 mmol) and 2.20 g (3.38 mmol)  $\text{Re}_2(\text{CO})_{10}$  were heated in a Carius tube at 190-195° for 10 hours. After removing volatiles, the residual solid was extracted with 50 ml n-hexane. Removal of n-hexane at reduced pressure followed by sublimation at room temperature gave a mixture of  $\text{Cl}_2\text{HSiRe}(\text{CO})_5$  and





$\text{Cl}_3\text{SiRe}(\text{CO})_5$ . Repeated fractional sublimations and recrystallizations did not yield pure  $\text{Cl}_2\text{HSiRe}(\text{CO})_5$ .

The solid not extracted by n-hexane was crystallized from dichloromethane to yield 0.10 g (3.3%) of  $[\text{Cl}_2\text{SiRe}(\text{CO})_4]_2$ . On other occasions, yields from this reaction under apparently similar conditions fell in the range 0.3% to 1.8%.

Di- $\mu$ -dichlorosilicon-bis(tetracarbonyliron),  
 $[\text{Cl}_2\text{SiFe}(\text{CO})_4]_2$ .

A mixture of  $\text{Fe}_3(\text{CO})_{12}$  (1.90 g, 3.77 mmol) and dichlorosilane (2.0 g, 19.8 mmol) was heated for 3 hours at  $85^\circ$ . After removal of volatiles, the remaining dark-brown solid was crystallized from dichloromethane ( $-80^\circ$ ) to afford pale-yellow crystals; (1.0 g, 33%) of  $[\text{Cl}_2\text{SiFe}(\text{CO})_4]_2$ .

Dichlorosilyl( $\pi$ -cyclopentadienyl)dicarbonyliron,  
 $\text{Cl}_2\text{HSiFe}(\text{CO})_2\text{Cp}$ .

A Carius tube containing dichlorosilane (1.0 g, 9.9 mmol) and  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  (2.24 g, 6.33 mmol) was heated for 12 hours at  $130^\circ$ . Removal of excess dichlorosilane and sublimation at  $50^\circ$  gave a yellow solid which infrared and mass spectroscopy showed to be a mixture of  $\text{Cl}_3\text{SiFe}(\text{CO})_2\text{Cp}$  and  $\text{Cl}_2\text{HSiFe}(\text{CO})_2\text{Cp}$  (the trichloro compound  $\text{Cl}_3\text{SiFe}(\text{CO})_2\text{Cp}$  is well characterized).<sup>1,8</sup> Repeated fractional





recrystallizations and sublimations afforded no pure  $\text{Cl}_2\text{HSiFe(CO)}_2\text{Cp}$ .

$\mu$ -[Phenyl(tetracarbonylcobalt)germanium]- $\mu$ -carbonyl-bis(tri-carbonylcobalt),  $\text{PhSiCo}_3(\text{CO})_{11}$ .

A solution of  $\text{Co}_2(\text{CO})_8$  (3.52 g, 10.3 mmol) and phenylsilane (0.74 g, 6.85 mmol) in 5 ml n-hexane was stirred at room temperature for 24 hours. Cooling the reaction mixture to  $-20^\circ$  gave black crystals. Recrystallization from n-hexane afforded dark-red crystals (1.5 g, 38%) of the product.



TABLE III

# COLORS, MELTING POINTS AND ANALYTICAL DATA OF SILICON-TRANSITION METAL CARBONYLS

Compound	Color	MP	Calculated %			Found %		
			C	H	Other	C	H	Other
Cl <sub>2</sub> HSiMn(CO) <sub>5</sub>	white	35-37	20.36	0.34	Cl, 24.04	20.86	0.27	Cl, 24.33
Me <sub>2</sub> HSiMn(CO) <sub>5</sub>	pale-yellow	liquid	33.08	2.78	-	33.86	3.05	-
Me <sub>2</sub> BrSiMn(CO) <sub>5</sub> <sup>a</sup>	white	53-55	25.24	1.81	Br, 23.99	25.43	1.75	Br, 23.85
trans-Ph <sub>2</sub> HSiMn(CO) <sub>4</sub> PPh <sub>3</sub>	white	115-118	66.67	4.28	Mn, 8.97	66.39	4.79	Mn, 8.96
Cl <sub>2</sub> Si[Mn(CO) <sub>5</sub> ] <sub>2</sub>	pale-yellow	98-100	24.57	0.00	Cl, 14.80	24.72	0.15	Cl, 14.83
[Me <sub>2</sub> SiMn(CO) <sub>4</sub> ] <sub>2</sub>	pale-yellow	>105 dec	32.01	2.75	Mn, 24.86	30.34	2.90	Mn, 24.76
[Me <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	pale-yellow	>140 dec	20.22	1.70	-	20.24	1.64	-
[Ph <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	yellow	>225 dec	39.99	2.10	-	39.86	2.17	-
[Cl <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	white	>185 dec	12.10	0.00	Cl, 17.85	11.96	0.29	Cl, 17.98
[Et <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	pale-yellow	128-130	25.00	2.62	-	24.72	2.59	-
(Me <sub>2</sub> Si) <sub>3</sub> Fe <sub>2</sub> (CO) <sub>6</sub>	yellow	>165 dec	31.73	3.99	-	31.06	3.61	-
PhSiCo <sub>3</sub> (CO) <sub>11</sub> <sup>b</sup>	dark-red	> 63 dec	34.59	0.85	Co, 29.95	34.78	1.14	Co, 26.12
continued.....								
48.								



FOOTNOTES TO TABLE III

- a Mn: Calculated, 16.50; Found, 16.30. Si: Calculated, 8.43; Found 8.53.
- b Si: Calculated, 4.76; Found, 5.41.



TABLE IV

INFRARED CARBONYL STRETCHING FREQUENCY AND PROTON NMR DATA OF SILICON-TRANSITION

Compound	METAL CARBONYLS			NMR τ Values
	Infrared Carbonyl Stretching Frequencies <sup>a</sup>			
Cl <sub>2</sub> HSiMn(CO) <sub>5</sub> <sup>c</sup>	2114(3.7),	2051(1.2),	2028(10), 2014(6.0)	τ 3.50
(Me) <sub>2</sub> HSiMn(CO) <sub>5</sub> <sup>d</sup>	2104(1.0),	2004(8.9),	1996(10.0), 1964(1.1)	
(Me) <sub>2</sub> BrSiMn(CO) <sub>5</sub>	2105(1.5),	2039(0.9),	2016(7.5), 2007(10.0)	τ 8.95
Ph <sub>2</sub> HSiMn(CO) <sub>4</sub> PPh <sub>3</sub> <sup>e</sup>	2048(0.5),	1992(1.1),	1957(br 10.0) 1923(1.0)	
Cl <sub>2</sub> HSiRe(CO) <sub>5</sub> <sup>f</sup>	2128(1.0),	2029(10.0),	2023(8.9)	τ 3.10
Cl <sub>2</sub> Si[Mn(CO) <sub>5</sub> ] <sub>2</sub>	2096(3.9), 2013(3.3),	2050(2.0), 1997(5.8)	2026(10.0), 2019(4.7),	
[Me <sub>2</sub> SiMn(CO) <sub>4</sub> ] <sub>2</sub>	2041(5.9),	2000(10.0),	1970(7.1), 1962(6.8)	τ 8.87
[Me <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	2061(5.0),	2004(10.0),	1977(br 8.2)	τ 8.75
[Ph <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	2068(5.1),	2010(10.0),	1986(7.8), 1984(8.1)	
[Cl <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	2087(4.9),	2033(10.0),	2001(7.1), 1995(7.3)	
[Et <sub>2</sub> SiRe(CO) <sub>4</sub> ] <sub>2</sub>	2059(4.9),	2001(10.0),	1975(7.5 br)	
Cl <sub>2</sub> HSiFe(CO) <sub>2</sub> Cp <sup>g</sup>	2028(7.9),	2020(9.8),	1980(8.2), 1971(10.0)	
(Me <sub>2</sub> Si) <sub>3</sub> Fe <sub>2</sub> (CO) <sub>6</sub>	2012(8.7),	1975(10.0)		τ 8.80
continued.....				

continued.....





TABLE IV (continued)

PhSiCo <sub>3</sub> (CO) <sub>11</sub>	2105(2.1), 2037(9.3), 1848(2.2)	2085(9.9), 2028(8.1),	2057(10.0), 2014(6.6),	2045(3.7), 1996(2.4)
Ph <sub>2</sub> SiCo <sub>2</sub> (CO) <sub>7</sub>	2092(8.7), 2016(8.9),	2056(10.0), 2003(5.0),	2036(9.5), 1837(7.5)	2024(7.0),

a Cyclohexane solutions, frequencies in cm<sup>-1</sup>. Figures in parentheses are relative band heights on a transmittance scale; br = broad, sh = shoulder.

b CDCl<sub>3</sub> solutions, TMS as internal standard.

c Si-H stretching mode at 2143 cm<sup>-1</sup> (broad, weak).

d Si-H stretching mode at 2085 cm<sup>-1</sup> (broad, weak).

e Si-H stretching mode at 2080 cm<sup>-1</sup> (broad, weak).

f Si-H stretching mode at 2140 cm<sup>-1</sup> (broad, weak).

g Not obtained pure but characterized mass spectroscopically.



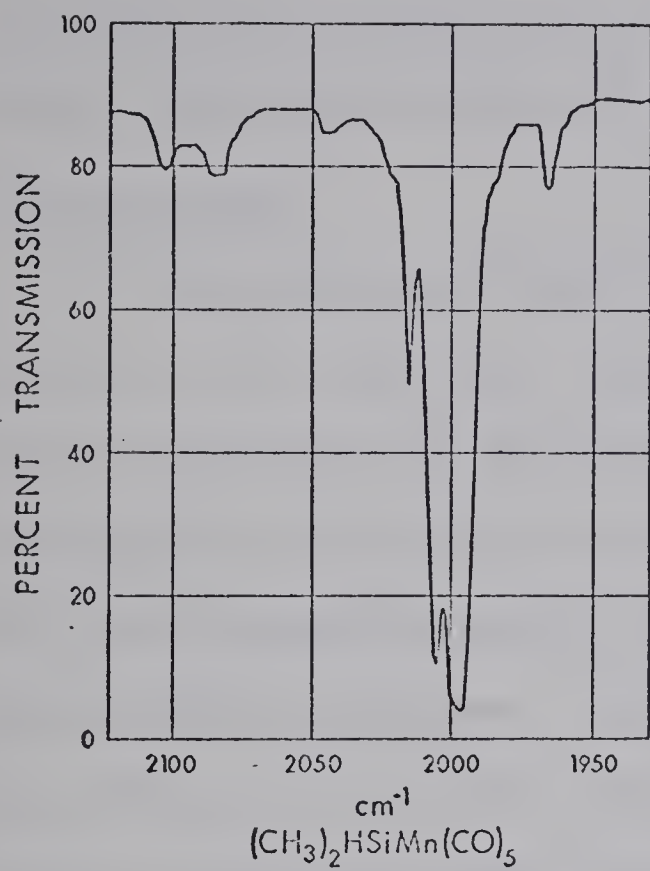


FIGURE 13

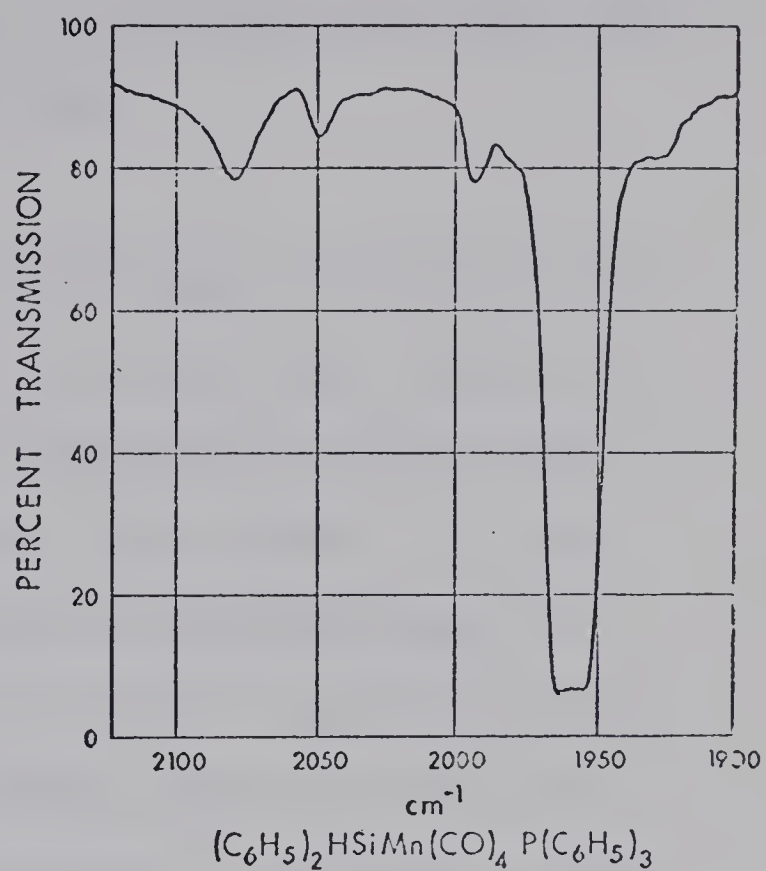


FIGURE 14

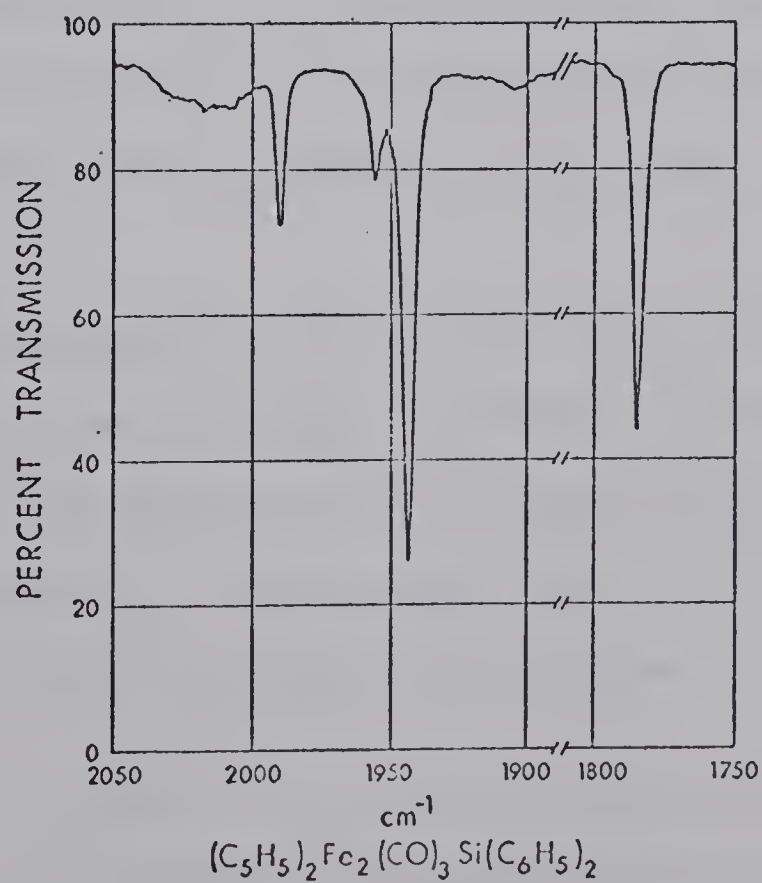


FIGURE 15



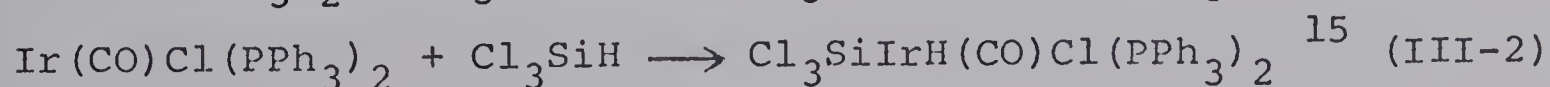
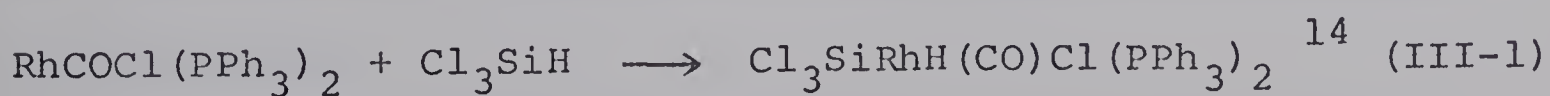
## CHAPTER III

### SYNTHESIS AND PROPERTIES OF SOME SILICON-BRIDGED METAL CARBONYL HYDRIDES AND RELATED COMPOUNDS.

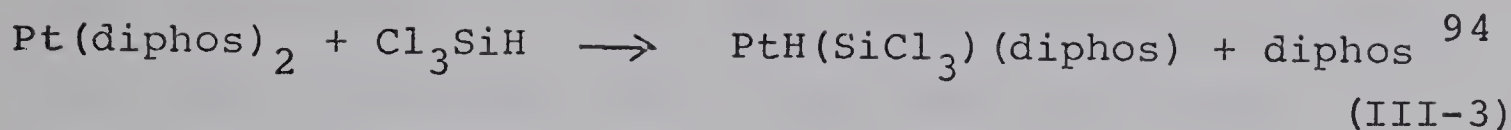
#### Introduction

The previous Chapter has shown that the thermal reaction of di- and tri- functional silanes with transition metal carbonyls is an effective method for synthesizing polynuclear transition metal silyl derivatives. In some of these reactions silyl hydrides can be postulated as intermediate species. Under less forcing conditions than the thermal reactions, possibilities exist for the isolation of some of these 'intermediates'. A possible route is ultraviolet irradiation at room temperature. This Chapter will describe the preparation by ultraviolet irradiation of some binuclear silyl transition-metal hydrides of rhenium, tungsten and molybdenum and of some related compounds.

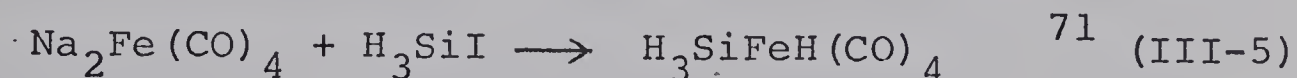
Until very recently there were only a few examples of silyl-substituted carbonyl hydrides of transition metals; these have been synthesized by various methods. Oxidative addition and oxidative elimination have yielded some silylhydrides of rhodium, iridium and platinum



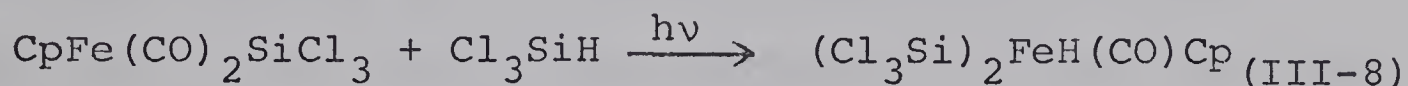
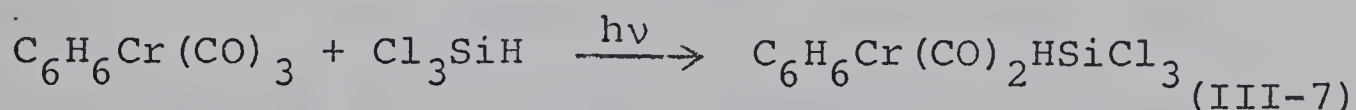
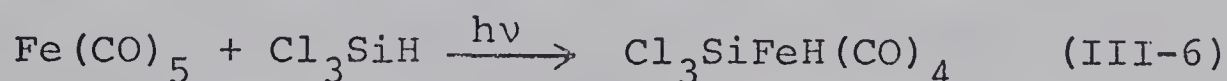




Other reactions which have been reported to yield silylhydrides are:



Almost concurrent to the present work, a series of mononuclear transition metal silylhydrides has been synthesized in this laboratory by W. Jetz; they were obtained from photochemical silane reactions.<sup>1,66,67</sup> Some examples are:



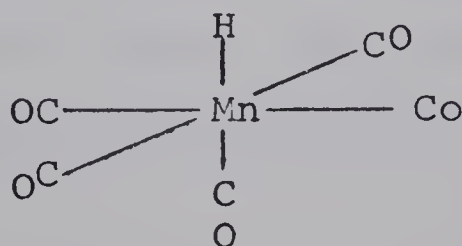
Similar mononuclear silylhydrides have been prepared in the present work and will be described in Chapter V. The present Chapter deals with the novel products obtained from the photochemical reactions of difunctional silanes,  $\text{R}_2\text{SiH}_2$ , with the carbonyls of rhenium, tungsten and molybdenum. The most interesting aspect of these complexes is the nature of attachment of the hydrogens to the transition metals.

Transition metal carbonyl hydrides have been known



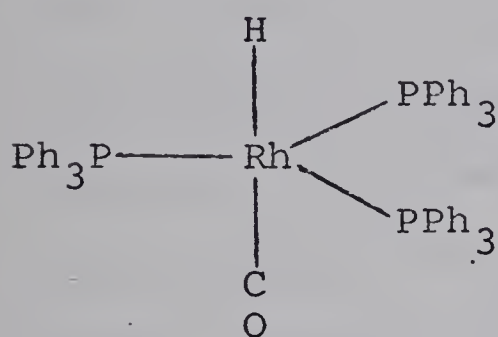
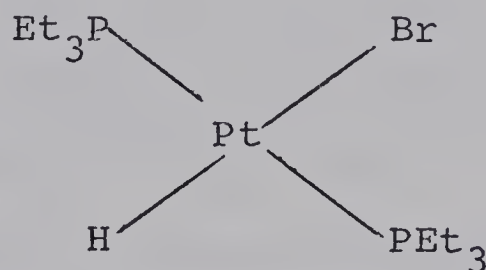


since the 1930's,<sup>96,97</sup> but their characteristic features have been established only in the last 10-15 years. An nmr proton resonance at high field was first observed for the transition metal hydride  $\text{HReCp}_2$  ( $\tau$  22.8) by Birmingham and Wilkinson in 1955.<sup>98</sup> Since this initial report, high field proton nmr resonance in the  $\tau$  15-35 region have become established as a characteristic feature of a hydrogen bonded to a transition metal. To account for the highly shielded nature of these protons many workers have postulated or calculated very short metal-hydrogen bond lengths. In fact, in 1942 Hieber<sup>99</sup> had suggested that the hydrogen atom was "buried" in the metal orbitals and was not a stereochemically active ligand in carbonyl hydrides such as  $\text{HCo(CO)}_4$ <sup>96,97</sup> and  $\text{H}_2\text{Fe(CO)}_4$ .<sup>96,5</sup> It was not until 1969 that Ibers et al<sup>100</sup> firmly established, from an X-ray and neutron diffraction study on  $\text{HMn(CO)}_5$ , that the hydrogen atom occupies a definite coordination site around the metal and that the metal-hydrogen distance ( $1.60 \text{ \AA}$ ) is that expected for a normal covalent bond.

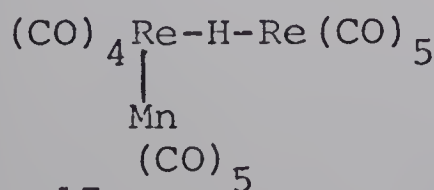
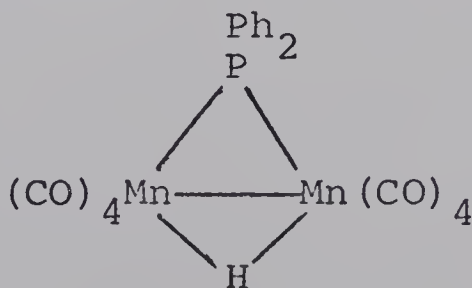




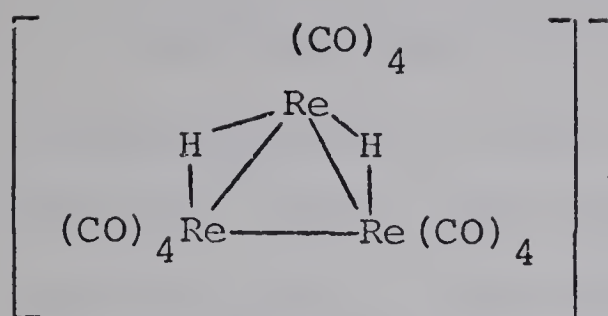
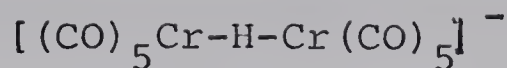
X-ray crystal structure determinations on compounds such as  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ ,<sup>101</sup> 15,  $\text{HPt}(\text{PEt}_3)\text{Br}$ ,<sup>102</sup> 16,  $\text{HOsBr}(\text{CO})(\text{PPh}_3)_3$ ,<sup>103</sup> and  $\text{H}(\text{Cl}_3\text{Si})_2\text{Fe}(\text{CO})\text{CP}$ <sup>104</sup> indicate that hydrogen occupies a distinct coordination site on the metal. Although the hydrogen atoms were not located with any certainty in these complexes, the arrangement of the other ligands suggested the most probable sites.

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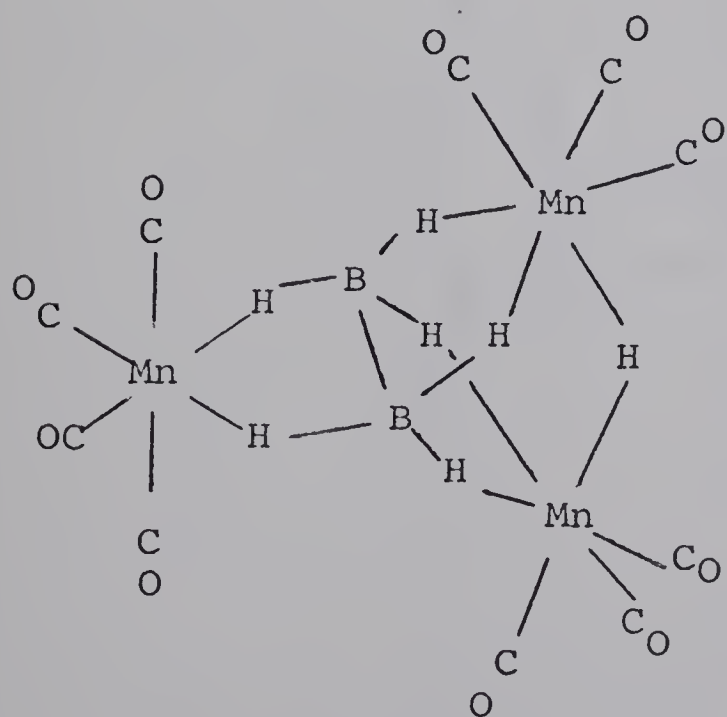
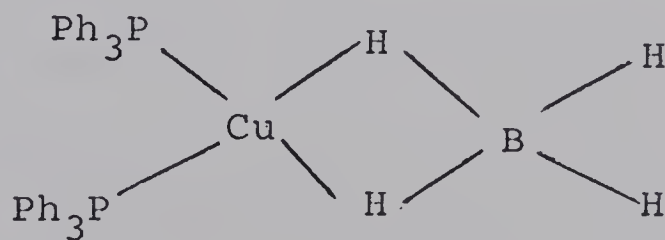
Many of the polynuclear transition metal hydrides appear to have the hydrogens located in bridging positions. The structure determinations of  $\text{HMnRe}_2(\text{CO})_{14}$ ,<sup>105</sup> 17,  $(\text{PPh}_2)\text{HMn}_2(\text{CO})_8$ ,<sup>106</sup> 18,  $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^\ominus$ ,<sup>107</sup> 19 and  $[\text{HCr}_2(\text{CO})_{10}]^\ominus$ ,<sup>108</sup> 20, suggested that the hydrogens were in bridging positions between two transition metals; as above, the hydrogen atom positions were not actually observed.

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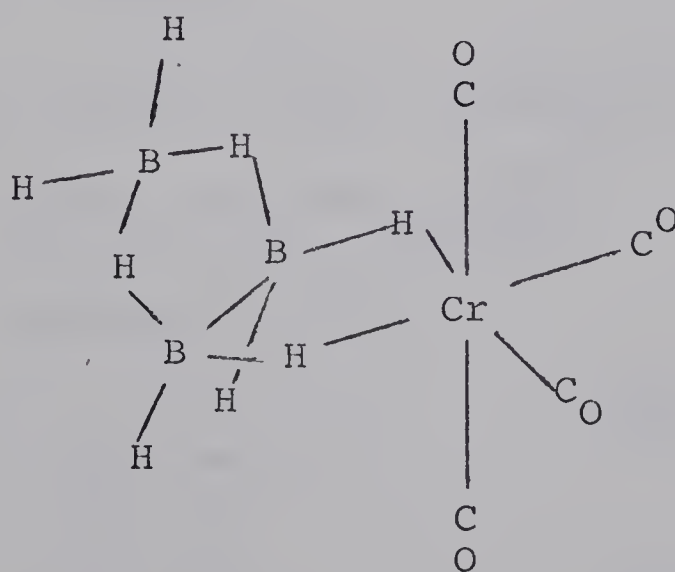
19  
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The four examples above represent both linear and bent bridges. Bridging hydrogens between a main group element and a transition metal have been known only for boron. The bridging hydrogens have been located in the complexes  $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ ,<sup>109</sup> 21,  $(\text{Ph}_3\text{P})_2\text{CuBH}_4$ ,<sup>110</sup> 22, and  $[\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8]^-$ ,<sup>111</sup> 23. The complex 21 contains hydrogen bridges between a main group and transition element (Mn-B) and also a hydrogen bridging two transition atoms.

21  
~~22  
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The compounds to be described in this Chapter appear to have hydrogen bridges which are related to the types discussed above. The properties of the complexes  $\text{H}_2\text{Re}_2(\text{CO})_8$  and  $\text{HClRe}_2(\text{CO})_8$ , which were prepared in the present study, strongly indicate bridging hydrogens between the rhenium atoms. For the silylmetal hydride complexes, there is some evidence for hydrogen bridges between silicon and the transition metal; however, at present, the existence of these bridges cannot be completely proved. The preparation and properties of these hydrides will now be given.





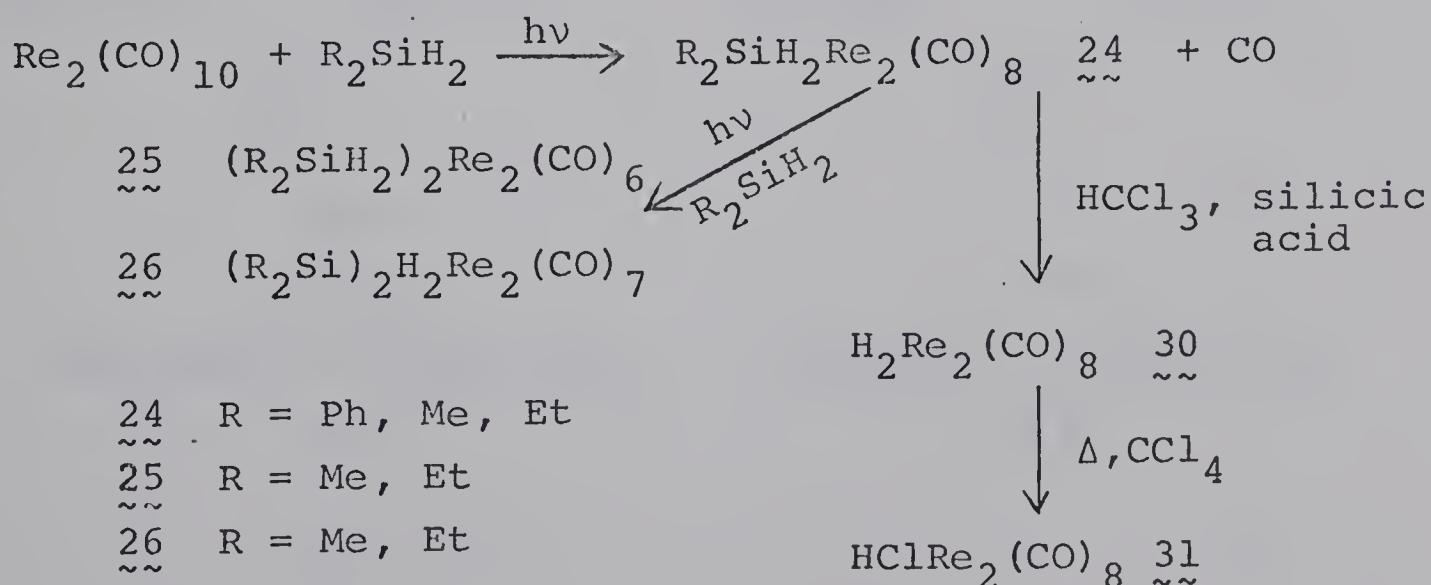


# R E S U L T S   A N D   D I S C U S S I O N

## 1. Synthesis

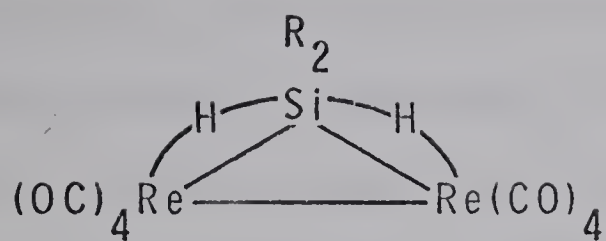
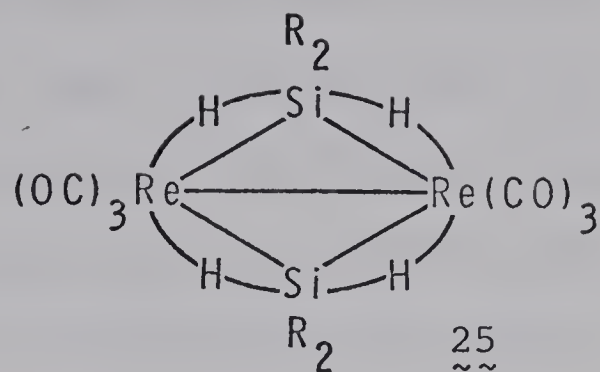
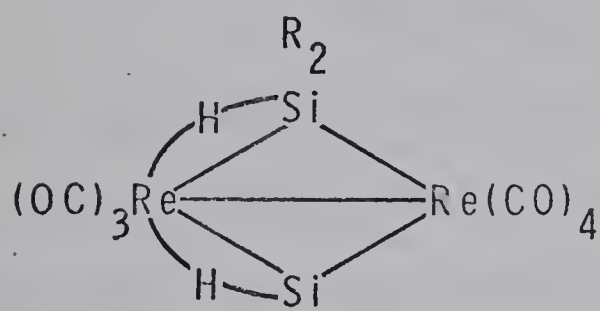
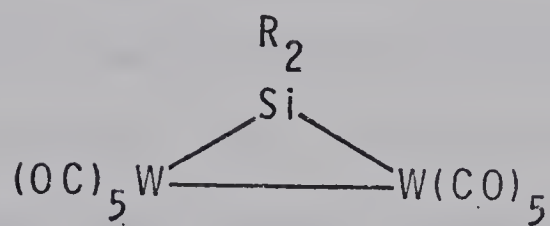
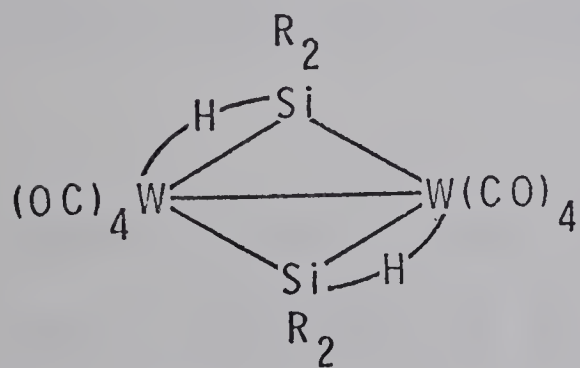
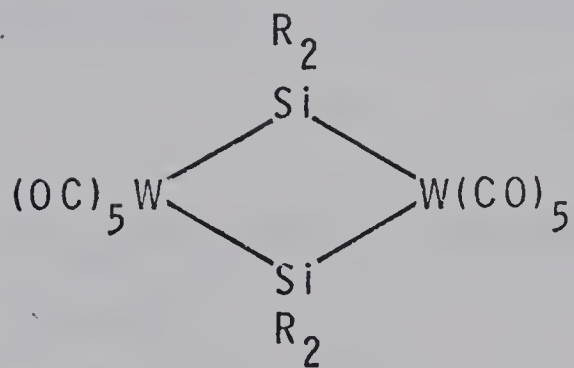
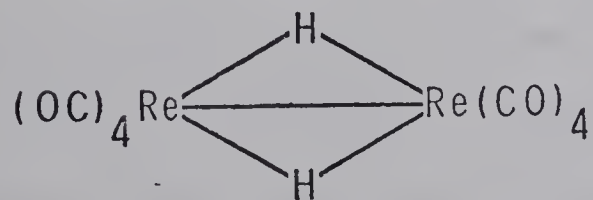
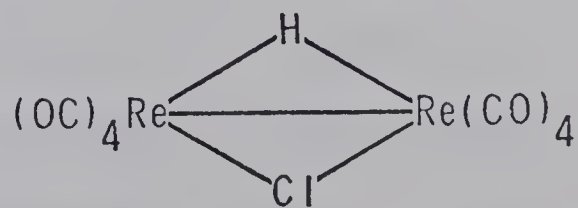
The ultraviolet irradiation of the difunctional silanes,  $R_2SiH_2$ , with the carbonyls of rhenium and tungsten resulted in the formation of a variety of novel dinuclear rhenium-silicon and tungsten-silicon compounds. Six types of complexes were obtained of which four contained transition-metal bonded hydrogens. Two new non-silicon containing compounds,  $H_2Re_2(CO)_8$  and  $HClRe_2(CO)_8$ , were also prepared during the course of this investigation. These eight complex types are formulated as shown in 24 to 31. Details of the structures and the formulations will be presented in the following sections.

The reactions of rhenium carbonyl are outlined in the following scheme:



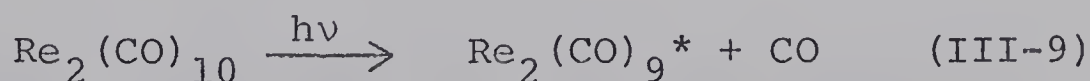
All ultraviolet irradiations were carried out in



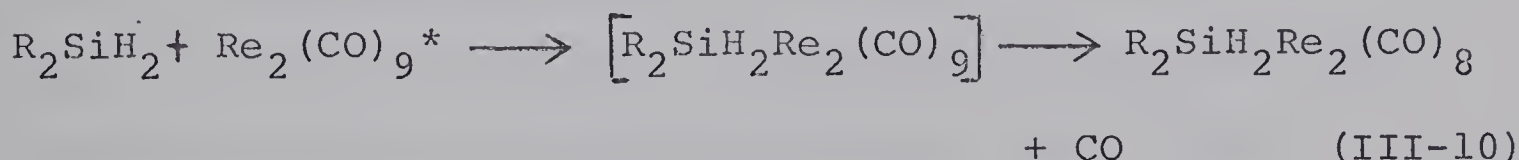
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hydrocarbon solvents (benzene, hexane or cyclohexane) while monitoring the progress of the reactions using infrared spectroscopy. Compounds of the type  $R_2SiH_2Re_2(CO)_8$ , 24, were obtained using a slight excess of the silane. Initially in these reactions a sufficiently energetic photon presumably ejects a CO to form the intermediate  $Re_2(CO)_9^*$ .



This intermediate then apparently reacts with the silane to form  $R_2SiH_2Re_2(CO)_9$ , but it appears that complexes of this type are very unstable under the reaction conditions and readily loses CO to afford  $R_2SiH_2Re_2(CO)_8$ .



However, species such as  $Cl_3SiHRe_2(CO)_9$  can be isolated and are discussed in the next Chapter.

The complexes  $(R_2SiH_2)_2Re_2(CO)_6$ , 25, and  $(R_2Si)_2H_2Re_2(CO)_7$ , 26, were obtained by irradiating  $Re_2(CO)_{10}$  with two to tenfold excesses of the silanes. Irradiation times were longer than that used for obtaining  $R_2SiH_2Re_2(CO)_8$ . These two types were obtained only with  $Me_2SiH_2$  and  $Et_2SiH_2$ ; no evidence for their formation from  $Ph_2SiH_2$  was found even on prolonged irradiation with excess silane. Infrared examination during the course



of the reactions suggested that  $(R_2SiH_2)_2Re_2(CO)_6$  and  $(R_2Si)_2H_2Re_2(CO)_7$  were being formed from  $R_2SiH_2Re_2(CO)_8$ , and that their direct formation from starting materials was a minor process if it occurred at all. It was shown that a pure sample of  $Et_2SiH_2Re_2(CO)_8$  was converted to  $(Et_2SiH_2)_2Re_2(CO)_6$  and  $(Et_2Si)_2H_2Re_2(CO)_7$  when irradiated with  $Et_2SiH_2$ .

The compounds  $(R_2SiH_2)_2Re_2(CO)_6$  and  $(R_2Si)_2H_2Re_2(CO)_7$  were always formed together, although varying the reaction conditions gave varying relative amounts of the two complexes. The yield of  $(R_2Si)_2H_2Re_2(CO)_7$  relative to  $(R_2SiH_2)_2Re_2(CO)_6$  increased when the reaction was carried out in a closed vessel where CO was allowed to build up; when the reaction was done at atmospheric pressure with nitrogen bubbling through the solution, very little  $(R_2Si)_2H_2Re_2(CO)_7$  resulted.

The complex  $H_2Re_2(CO)_8$  was obtained by stirring a pure sample of  $R_2SiH_2Re_2(CO)_8$  in a chloroform-silicic acid mixture. Attempts were made to determine the fate of the  $R_2Si$  moiety, but were unfruitful. The complex  $H_2Re_2(CO)_8$  was first obtained in low yields from the thermal reaction of  $Me_2SiH_2$  and  $Re_2(CO)_{10}$  (Chapter II) when purification of  $[Me_2SiRe(CO)_4]_2$  by chromatography on silicic acid was attempted. Examination of the reaction mixture (from thermolysis) revealed that small











Tungsten hexacarbonyl was much less reactive than rhenium carbonyl; in all the reactions performed, at least half the tungsten hexacarbonyl remained unreacted even on prolonged irradiation (see Experimental). No evidence for the phenyl analogs of  $\sim\sim$  28 and  $\sim\sim$  29 was obtained. Again the relative yields of these two complexes were dependent upon CO pressure and very low yields of  $(R_2Si)_2H_2W_2(CO)_8$  were obtained with  $Me_2SiH_2$  where the volatility of the silane (bp =  $-20^\circ$ ) required the use of a closed vessel. Molybdenum hexacarbonyl reacted in an analogous manner;  $Ph_2SiMo_2(CO)_{10}$  and  $(Et_2Si)_2H_2Mo_2(CO)_8$  have been obtained but  $(R_2Si)_2Mo_2(CO)_{10}$  has not been isolated or detected spectroscopically.

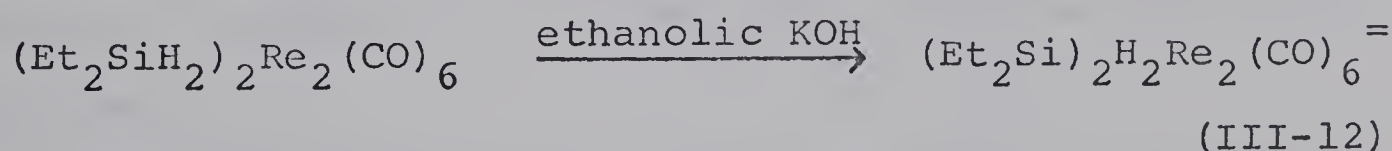
During the irradiations of tungsten hexacarbonyl with the silanes  $R_2SiH_2$ , no evidence appeared for the existence of a mononuclear species  $R_2SiH_2W(CO)_5$ . An anomalous result during the course of these silane reactions with metal carbonyl in this laboratory has been the failure of  $W(CO)_6$  to react either thermally<sup>112</sup> or under ultraviolet irradiation<sup>113</sup> with  $Cl_3SiH$  or  $R_3SiH$ .

The mode of formation of  $(R_2Si)_2W_2(CO)_{10}$  and  $(R_2Si)_2H_2W_2(CO)_8$  from  $R_2SiW_2(CO)_{10}$  is unclear. In the formation of  $(R_2Si)_2W_2(CO)_{10}$  the net result is the insertion of an  $R_2Si$  group into the tungsten-tungsten bond of  $R_2SiW_2(CO)_{10}$ . This is reminiscent of the insertion of  $GeI_2$  into  $[W_2(CO)_{10}]^-$  to yield  $[I_2GeW_2(CO)_{10}]^-$ .<sup>19</sup> It is



difficult to ascertain whether  $R_2Si$  is actually generated in the reaction mixture or if an unstable silylhydride intermediate is first formed which then decomposes to  $(R_2Si)_2W_2(CO)_{10}$ . The complex  $(R_2Si)_2H_2W_2(CO)_8$  appears to be formed by silane displacement of two carbonyls from  $R_2SiW_2(CO)_{10}$ ; however, the probable location of the two hydrogens (as inferred from the X-ray crystal structure) makes this process somewhat uncertain.

The success of Kaesz et al.<sup>107</sup> in forming the anions  $[H_2Re_3(CO)_{12}]^-$  and  $[HRe_3(CO)_{12}]^-$  by treatment of  $[HRe(CO)_4]_3$  with base stimulated similar deprotonation attempts on some of the hydrides discussed above. Preliminary attempts under similar conditions (ethanolic KOH) with  $H_2Re_2(CO)_8$ ,  $Ph_2SiH_2Re_2(CO)_8$ ,  $(Et_2Si)_2H_2W_2(CO)_8$  gave no isolable products. Only with  $(EtSiH_2)_2Re_2(CO)_6$  was an identifiable product obtained:



The deprotonation of mononuclear silylhydrides is discussed in Chapter V.

The complexes described above were characterized spectroscopically and by elemental analyses. The spectra and other properties of the various compound types are now discussed in relation to the structures and the bonding.





## 2. Spectral Properties and Structures

This section will recount the properties of the various rhenium and tungsten complexes whose synthesis has just been discussed. The formulations and structures will be inferred mainly from the various spectral data. X-ray crystallography in this department has confirmed the proposed formulations and structures for many of the complexes. Although the hydrogens were not located, the arrangement of the other atoms and supporting spectral data suggested the locations of the hydride ligands. These aspects of the various compound types (24-31) will now be discussed.

### Complexes $R_2SiH_2Re_2(CO)_8$

These complexes are moderately air-stable pale-yellow or white crystalline solids, soluble in hexane, carbon tetrachloride and benzene. In chloroform or dichloromethane, decomposition to  $H_2Re_2(CO)_8$  occurs as previously described.

The infrared spectra (in the carbonyl stretching region) of these complexes with various R groups are shown in Figures 16-19. These compounds all show similar carbonyl band patterns with 6 or 7 observable bands; a maximum of 7 carbonyl stretching bands is predicted for the  $C_{2v}$  molecular symmetry as found in the structure determination.<sup>68,114</sup> The carbonyl region of the deuterated der-





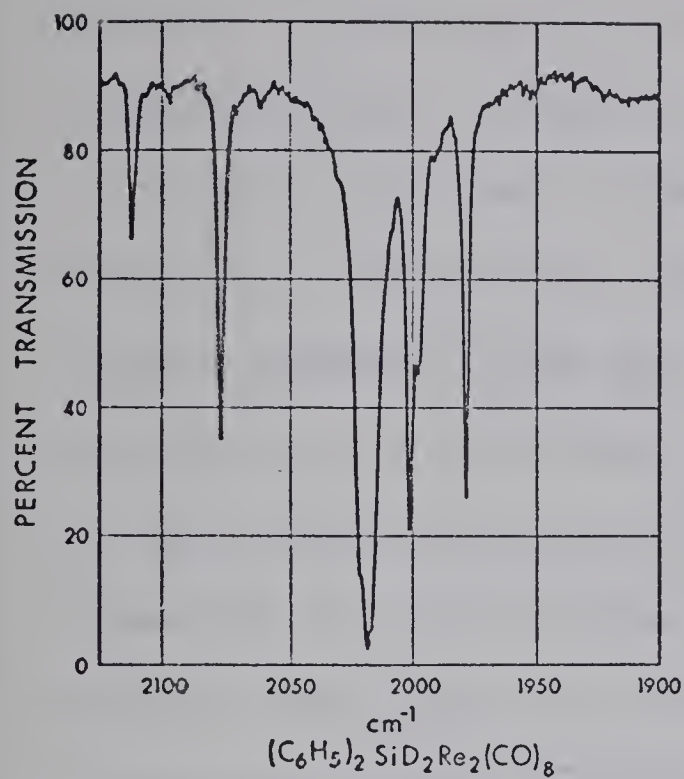


FIGURE 16

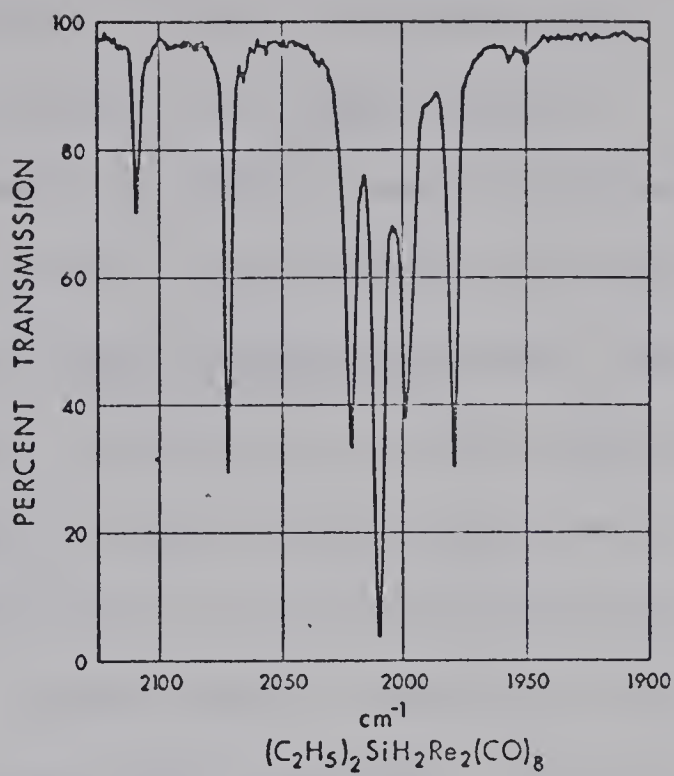


FIGURE 17

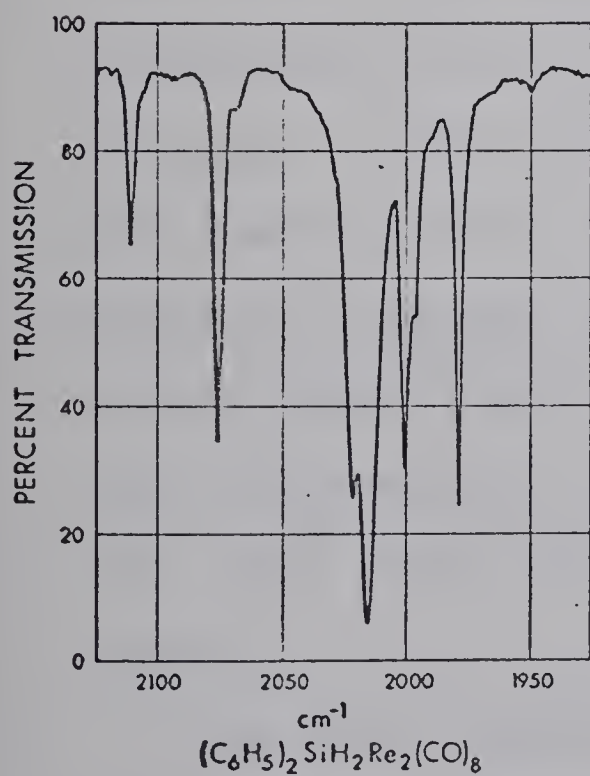


FIGURE 18

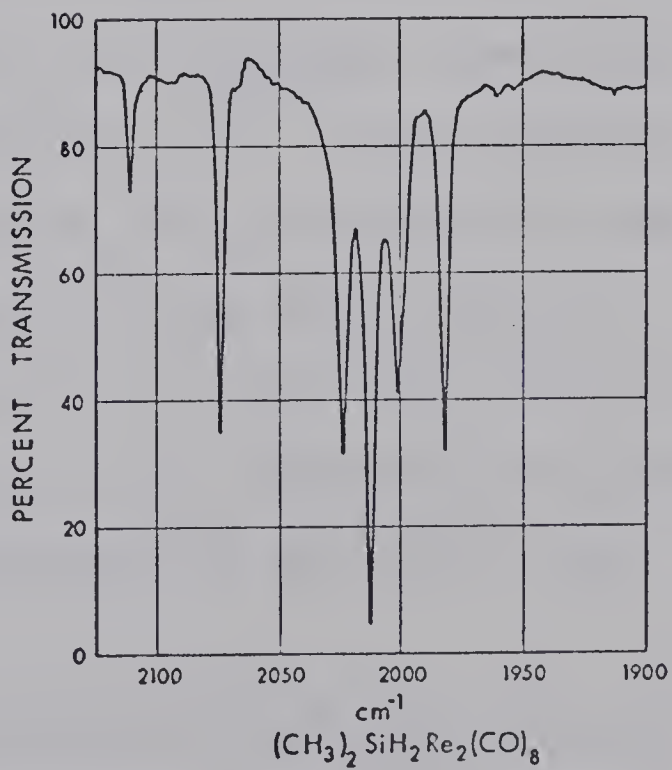


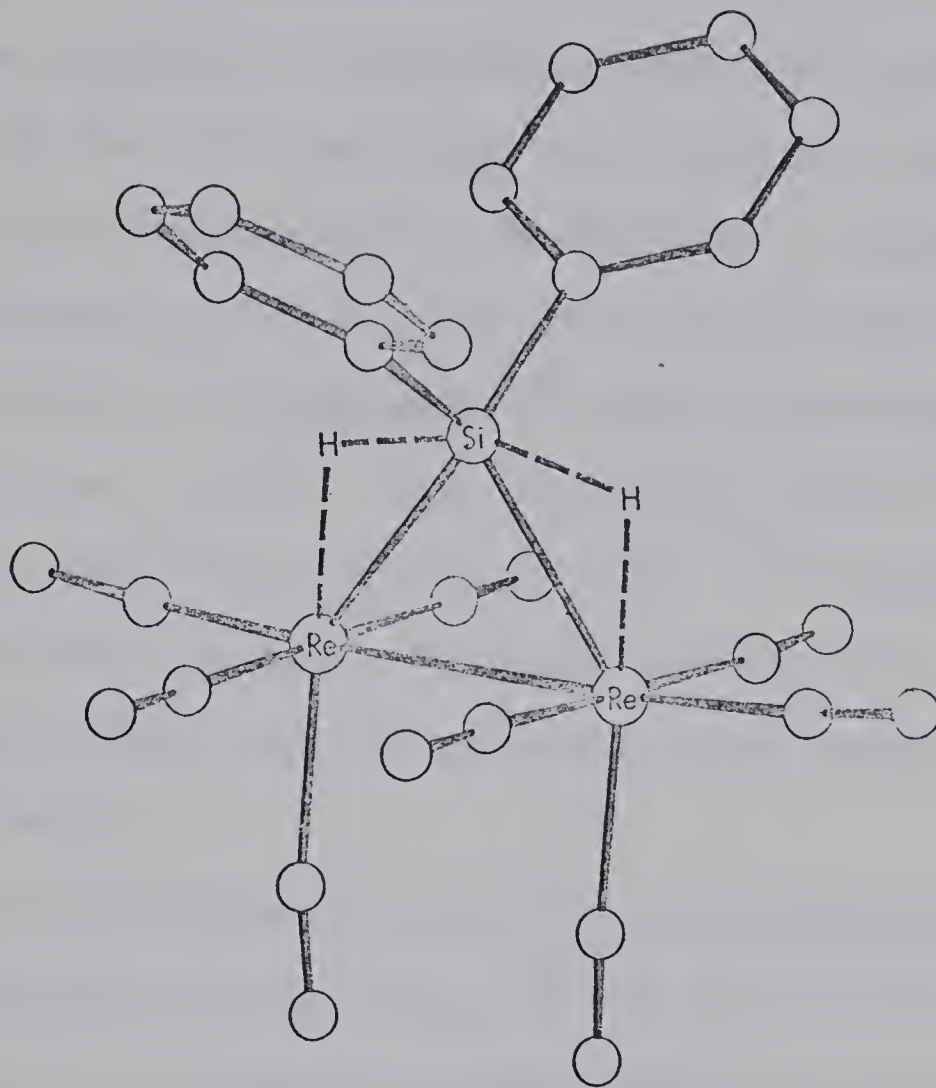
FIGURE 19



ivative  $\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$  (Figure 16) is unchanged from  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  (Figure 18) except for small shifts ( $< 3 \text{ cm}^{-1}$ ) in some of the band positions (see Experimental Section). Therefore, none of the bands in the carbonyl region appears to be due to a Re-H stretching mode, although it is conceivable that it could be buried under one of the strong carbonyl bands. Also, no new bands were observed in the infrared spectrum of the deuterated complex in the  $1600\text{--}1200 \text{ cm}^{-1}$  region where a terminal Re-D stretching frequency might have been expected. However, a Raman spectrum of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  showed a weak band at  $1785 \text{ cm}^{-1}$  which shifted to  $1282 \text{ cm}^{-1}$  in the deuteride<sup>115</sup> (the calculated value for the deuteride frequency is  $1263 \text{ cm}^{-1}$ ). The Raman band at  $1785 \text{ cm}^{-1}$  is in the neighborhood of the terminal Re-H infrared stretching frequency of  $1832 \text{ cm}^{-1}$  in  $\text{HRe}(\text{CO})_5$ .<sup>116</sup> This suggests that the Re-H bond in  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  resembles in some respects a covalent terminally bonded Re-H. Yet it differs from "normal" terminal metal-hydrogen bonds in that its stretching vibration is not observed in the infrared. This point will be discussed at the end of the Chapter.

The X-ray crystal structure of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  was determined in this department by M. Elder<sup>114</sup> and is shown in Figure 20; although the hydrogen atoms were





Bond Lengths

Re-Re	3.12 Å
Re-Si	2.54 Å

Bond Angles

Re-Si-Re	75.7°
Re-Re-Si	52.2°

Molecular Structure of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  <sup>114</sup>

FIGURE 20



not located, the unique pair are shown in the conspicuously vacant sixth coordination site (octahedral) of each rhenium atom. Nmr evidence is consistent with this placement (see below). If the hydrogen atoms are placed in the Re-Si-Re plane at right angles to the Re-Re bond as shown, and with a Re-H distance of 1.68 Å (the Re-H bond length found for  $\text{ReH}_9$  by neutron diffraction),<sup>117</sup> the silicon-hydrogen distance would be 1.59 Å. This distance, which is only 0.11 Å longer than the Si-H distance in  $\text{SiH}_4$ ,<sup>118</sup> suggests at least a weak attractive silicon-hydrogen interaction. Of course the hydrogen atoms may not actually be at right angles to the Re-Re bond.

The solid-state structure of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  bears some resemblance to  $\text{Re}_2(\text{CO})_{10}$ ,<sup>40</sup> but has an eclipsed conformation of the carbonyls necessitated by the bridging silicon. The slightly longer Re-Re bond length (3.12 Å vs 3.02 Å) could be partially due to the eclipsed conformation of the carbonyls. There are no significant differences in the Re-Si bond lengths when compared to the Re-Si lengths in  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$  (Figure 9); the latter has no hydride ligands. The structure of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  resembles the hydrogen-bridged anion  $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^\ominus$ ,<sup>107</sup> 19, where the  $\text{H}_2\text{Re}(\text{CO})_4^\ominus$  group is replaced by a  $\text{Ph}_2\text{SiH}_2$  group.

The nmr spectra of the complexes  $\text{R}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$







give further support to the proposed placement of the hydride ligands. Nmr signals in the  $\tau$  19-21 region were observed (see Table VIII); this is consistent with transition metal bonded protons. The integration confirmed the ratio of R group protons to high field protons. The methyl resonance of  $\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  appeared as a 1:2:1 triplet (centered at  $\tau$  8.87,  $J = 1.5$  Hz); irradiation at the broad high field resonance ( $\tau$  20.56) caused the methyl triplet to collapse to a sharp singlet. This  $A_6X_2$  pattern shows that the high-field protons are magnetically equivalent and most likely in symmetrically equivalent positions in the  $\text{SiRe}_2$  plane (this argument supposes that the magnetic equivalence is neither accidental nor the result of a rapid exchange process). The magnitude of the coupling constant  $J$ , when compared to the coupling of 4.2 Hz in dimethylsilane itself, suggests that the high-field protons are proximate to the dimethylsilicon group.

The mass spectra of the complexes  $\text{R}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  all showed the molecular ion with successive loss of eight carbonyl groups. Although the molecular ion showed little or no hydrogen loss, all other fragments in the series  $\text{R}_2\text{SiH}_2\text{Re}_2(\text{CO})_n^+$  ( $0 < n < 7$ ) showed considerable hydrogen loss. A more detailed discussion of the mass spectra of these hydrides is given in the mass spectral section.



### Complexes $(R_2SiH_2)_2Re_2(CO)_6$

These compounds are white, crystalline, air-stable solids which are very soluble in hydrocarbon solvents. Unlike the complexes  $R_2SiH_2Re_2(CO)_8$ , these are stable in chloroform and dichloromethane.

Their structure can be derived from the structure of  $R_2SiH_2Re_2(CO)_8$  (Figure 20) by replacing the pair of carbonyl groups trans to the  $R_2SiH_2$  moiety by another such group. Such a molecule would possess idealized  $D_{2h}$  molecular symmetry and three carbonyl stretching bands would be predicted; Figure 21 shows the infrared spectrum of  $(Et_2SiH_2)_2Re_2(CO)_6$ , which exhibits three bands. Analogous to the complexes  $R_2SiH_2Re_2(CO)_8$ , the complexes  $(R_2SiH_2)_2Re_2(CO)_6$  showed no infrared bands which could be assigned to a Re-H stretching mode (although in this case not confirmed by preparing the deuteride).

Although the molecular ion  $[(R_2SiH_2)_2Re_2(CO)_6]^+$  with all hydrogens intact was not observed, the nmr integration of the high-field protons (Table VIII) vs the R protons confirmed that four high-field protons were present.

The structure of  $(Et_2SiH_2)_2Re_2(CO)_6$  was determined in this department by M. Cowie and M. J. Bennett<sup>119</sup> and is shown in Figure 22. The structure shows the expected  $D_{2h}$  symmetry and is very closely related to that of  $Ph_2SiH_2Re_2(CO)_8$ . The Re-Re bond length of  $3.08 \text{ \AA}$  is



slightly shorter than the  $3.12 \text{ \AA}$  found for  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ . The Re-Si bond lengths and the Re-Si-Re bond angles are almost the same as found for  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ . By an argument similar to that used in the placement of the hydride ligands in  $\text{R}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ , the four hydride ligands in  $(\text{R}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  can be placed in the four positions bridging the Re-Si bonds (in the  $\text{Re}_2\text{Si}_2$  plane).

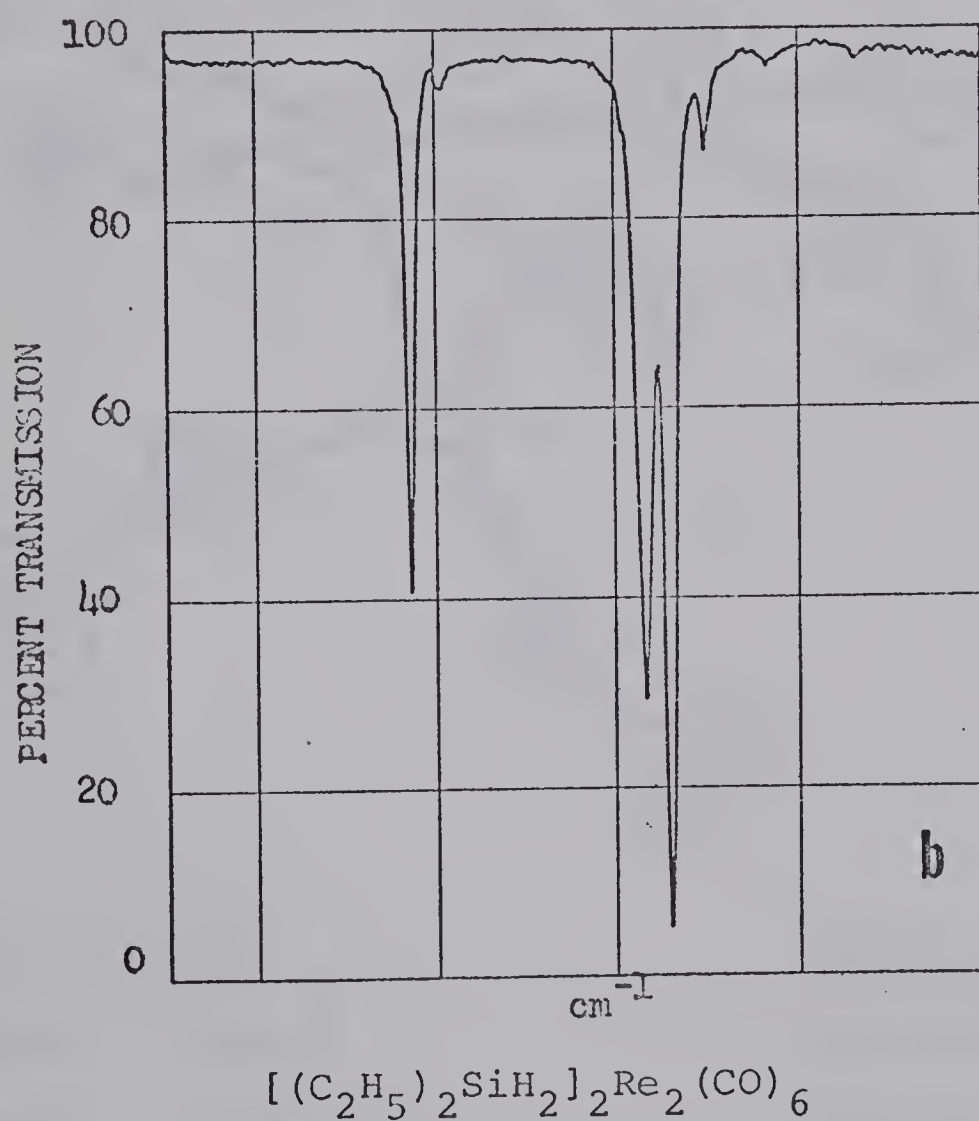
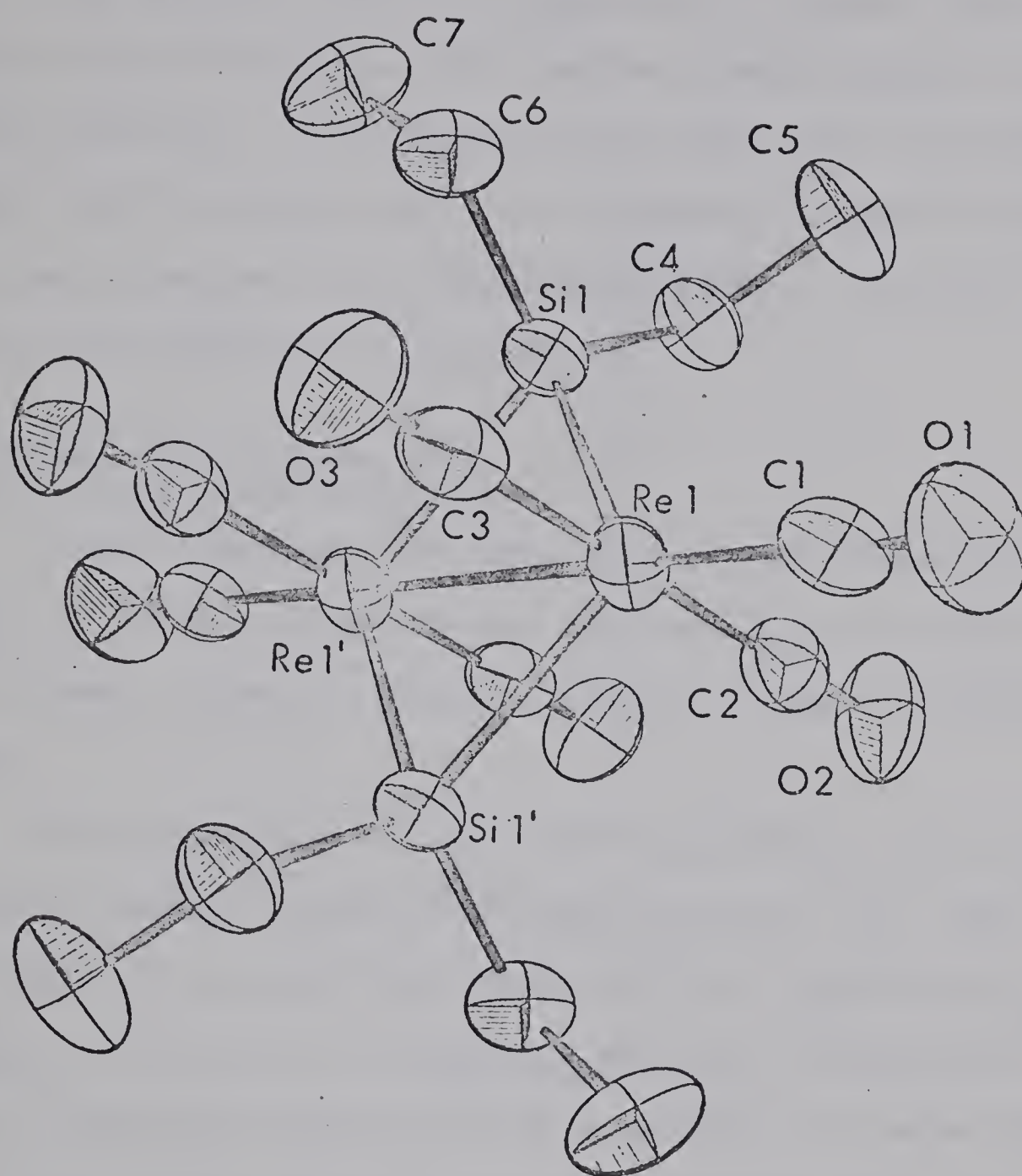


FIGURE 21







Bond Lengths

Re-Re	3.08 Å
Re-Si	2.53 Å

Bond Angles

Re-Si-Re	74.9°
Re-Re-Si	52.5°

Molecular Structure of  $(\text{Et}_2\text{SiH}_2)\text{Re}_2(\text{CO})_6$  <sup>119</sup>

FIGURE 22





The dianion  $[(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_6]^{2-}$  showed three carbonyl stretching bands, in a pattern very similar to the parent hydride. A structure consistent with the three bands would be obtained if two diagonally opposite protons were removed from  $(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$ . Such an anion would have idealized  $\text{C}_{2h}$  symmetry.

#### Complexes $(\text{R}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$

These complexes are also white-crystalline moderately air-stable crystals and very soluble and stable in most common organic solvents (benzene, hexane, chloroform).

The proposed structure has  $\text{C}_{2v}$  symmetry with the  $\text{C}_2$  axis running through the rhenium atoms, 32. This structure is obtained by taking half of  $[\text{R}_2\text{SiRe}(\text{CO})_4]_2$  (Figure 9) and half of  $(\text{R}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  (Figure 22). Such a structure would predict a maximum of seven carbonyl stretching bands; five bands are observed for  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  (Figure 23).

Table V shows the carbonyl stretching frequencies of  $[\text{Et}_2\text{SiRe}(\text{CO})_4]_2$ ,  $(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  and  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$ ; the frequencies of  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  somewhat resemble the frequencies of the other two compounds.



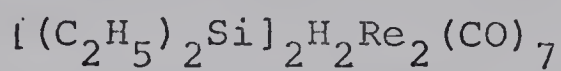
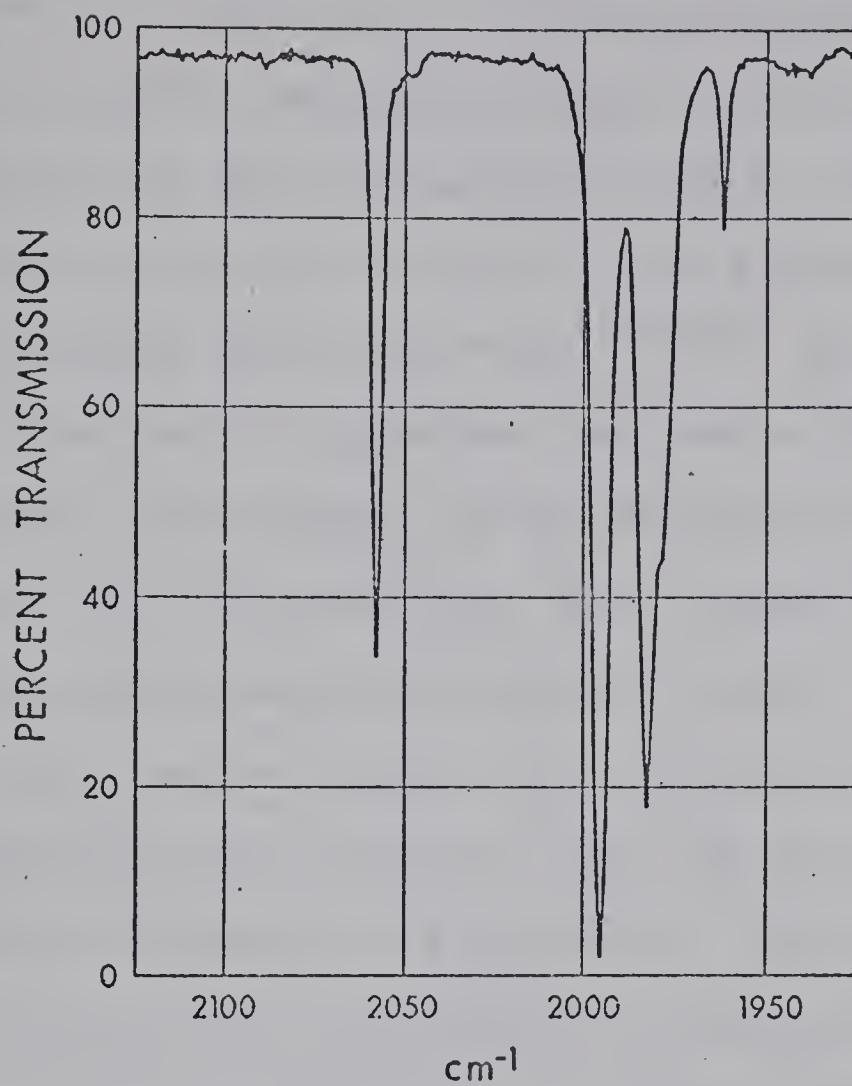


FIGURE 23

TABLE V

Carbonyl Stretching Frequencies of Some Diethylsilicon

Dirhenium Compounds

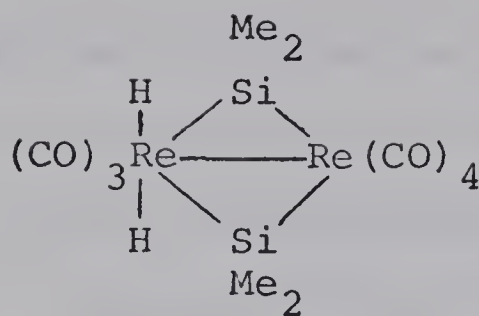
<u>Compound</u>	<u>Frequencies (cm<sup>-1</sup>)</u>			
$[Et_2SiRe(CO)_4]_2$	2059	2001		1975
$(Et_2SiH_2)_2Re_2(CO)_6$	2055	1991	1984	
$(Et_2Si)_2H_2Re_2(CO)_7$	2057	1994	1981	1977
				1959



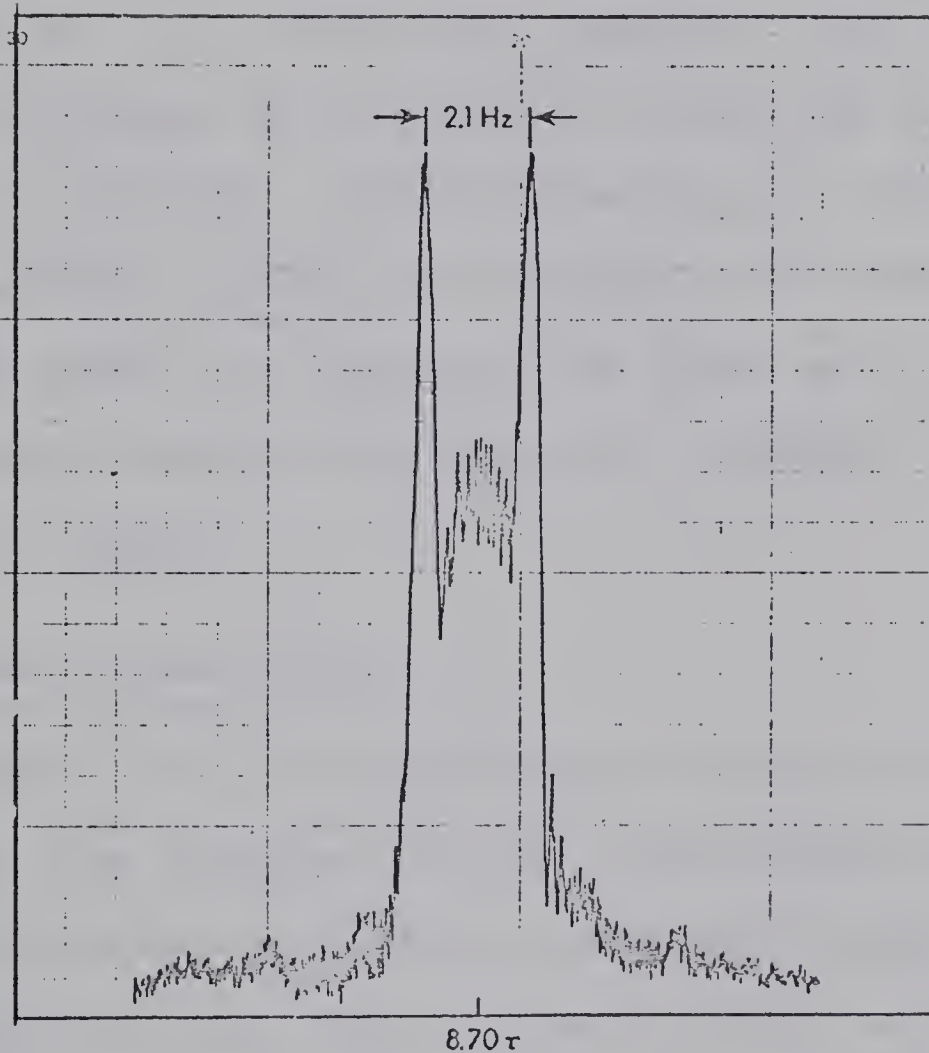
The nmr spectrum of  $(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  provides convincing support for the proposed  $\text{C}_{2v}$  structure. The complex resonance for the methyl protons is shown in Figure 24. This pattern is a form of the X spectrum of an  $\text{X}_6\text{AA}'\text{X}'_6$  system with  $J_{\text{XX}'} = 0$ .<sup>120,121</sup> The protons A and A' are chemically equivalent but are magnetically non-equivalent with respect to the X or X' protons as is expected for structure 32. This system is analogous to many bis(dimethylphenylphosphine) metal complexes,<sup>122</sup> where the A and A' nuclei are the two phosphorous atoms. The  $\text{X}_6\text{AA}'\text{X}'_6$  system exhibits (for the X part of the spectrum) a maximum of 13 pairs of lines symmetrically placed around the unperturbed X resonance.<sup>120</sup> The resonance is characterized by a strong doublet with a separation  $|J_{\text{AX}} + J_{\text{AX}'}|$ , the sum of the short and long range coupling constants, equal to 2.1 Hz in this case (Figure 24). If the value for the short range coupling is taken as 1.5 Hz (as found in  $\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ ), the long range coupling constant would be equal to 0.6 Hz provided that the signs for the two constants are the same. Irradiation at the broad, high-field resonance ( $\tau$  20.11) caused the methyl multiplet to collapse to a sharp singlet.

The X-ray crystal structure of  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  has recently been completed;<sup>123</sup> the anticipated  $\text{C}_{2v}$





32  
~~



Nmr spectrum at 100 MHz of the methyl protons of  
 $(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$

FIGURE 24





structure was found and is shown in Figure 25. The two hydride ligands can be placed in the two vacant sites in the  $\text{Re}_2\text{Si}_2$  plane on the three-carbonyl side. This side of the molecule is identical to half the molecule of  $(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  (Figure 22). The other side is the same as one half the molecule of the  $[\text{R}_2\text{SiRe}(\text{CO})_4]_2$  type (Figure 9). The Re-Re bond length of 3.05 Å is intermediate between Re-Re distances found for the complexes  $[\text{Et}_2\text{SiH}_2]_2\text{Re}_2(\text{CO})_6$  and  $[\text{Ph}_2\text{SiRe}(\text{CO})_4]_2$ . The silicon-rhenium bond lengths are essentially the same as found for the other two complexes and there are no significant differences between the hydrogen 'bridged' and 'non-bridged' bonds.

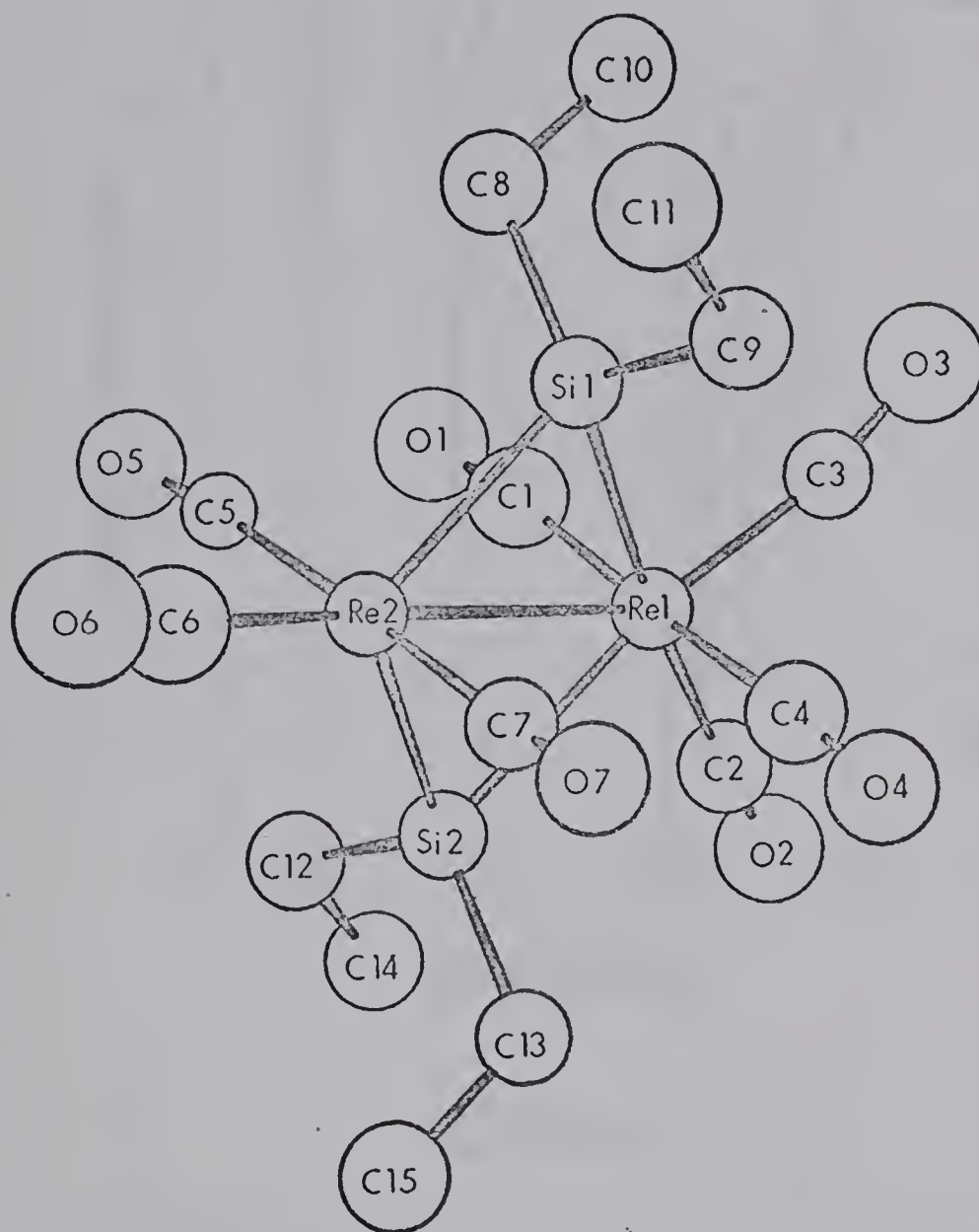
#### Complexes $\text{R}_2\text{SiW}_2(\text{CO})_{10}$

These are orange crystalline compounds which decompose on long storage to  $\text{W}(\text{CO})_6$  and unidentified products. In solution decomposition is much more rapid. The order of stabilities for the various R groups is  $\text{Ph} > \text{Et} > \text{Me}$ .

The mass spectra showed the molecular ion and peaks corresponding to the consecutive loss of ten carbonyls. The carbonyl stretching region of the infrared spectrum of  $\text{Ph}_2\text{SiW}_2(\text{CO})_{10}$  is shown in Figure 26; eight bands are observed.

The proposed structure for these complexes was shown in simplified form at the beginning of this Chapter, 27;





Molecular Structure of  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  <sup>123</sup>

Bond Lengths

Re-Re = 3.05 Å

Re-Si = 2.55 Å

Bond Angles

Re-Si-Re = 73.5°

Si(1)-Re(2)-C(6) = 128°

FIGURE 25



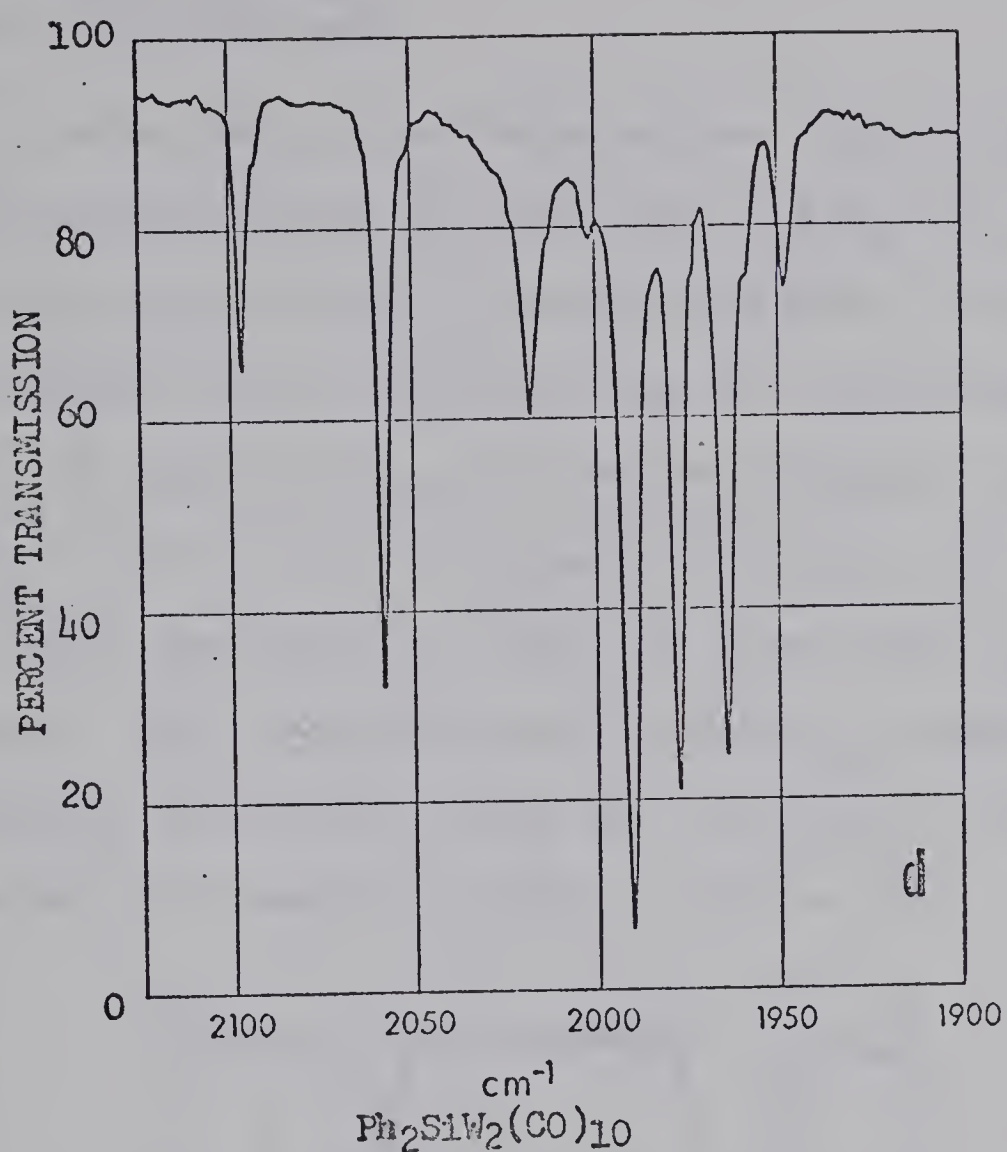


FIGURE 26

this involved seven-coordinate tungsten and the invoking of a W-W bond to conform to the effective atomic number rule. A detailed picture of the proposed structure can be constructed as follows: a  $W_2(CO)_{10}$  unit in an eclipsed manganese carbonyl arrangement with the bridging  $R_2Si$  group located in a staggered position with respect to the carbonyls. This structure would have  $C_{2v}$  symmetry and eight carbonyl stretching bands would be predicted ( $3A_1 + 2B_1 + 3B_2$ ).



Complex  $(\text{Me}_2\text{Si})_2\text{W}_2(\text{CO})_{10}$

This moderately air-stable yellow crystalline solid can be considered to be derived from  $\text{R}_2\text{SiW}_2(\text{CO})_{10}$  by inserting an  $\text{Me}_2\text{Si}$  moiety into the W-W bond. The proposed structure can be derived from the postulated structure of  $\text{R}_2\text{SiW}_2(\text{CO})_{10}$ ; the second bridging  $\text{Me}_2\text{Si}$  group would also be in a staggered position with respect to the radial carbonyls so that the four atoms  $\text{W}_2\text{Si}_2$  lie in a plane. This structure would have  $\text{D}_{2h}$  symmetry and four carbonyl stretching bands are predicted; four bands are observed for  $(\text{Me}_2\text{Si})_2\text{W}_2(\text{CO})_{10}$  (Figure 27).

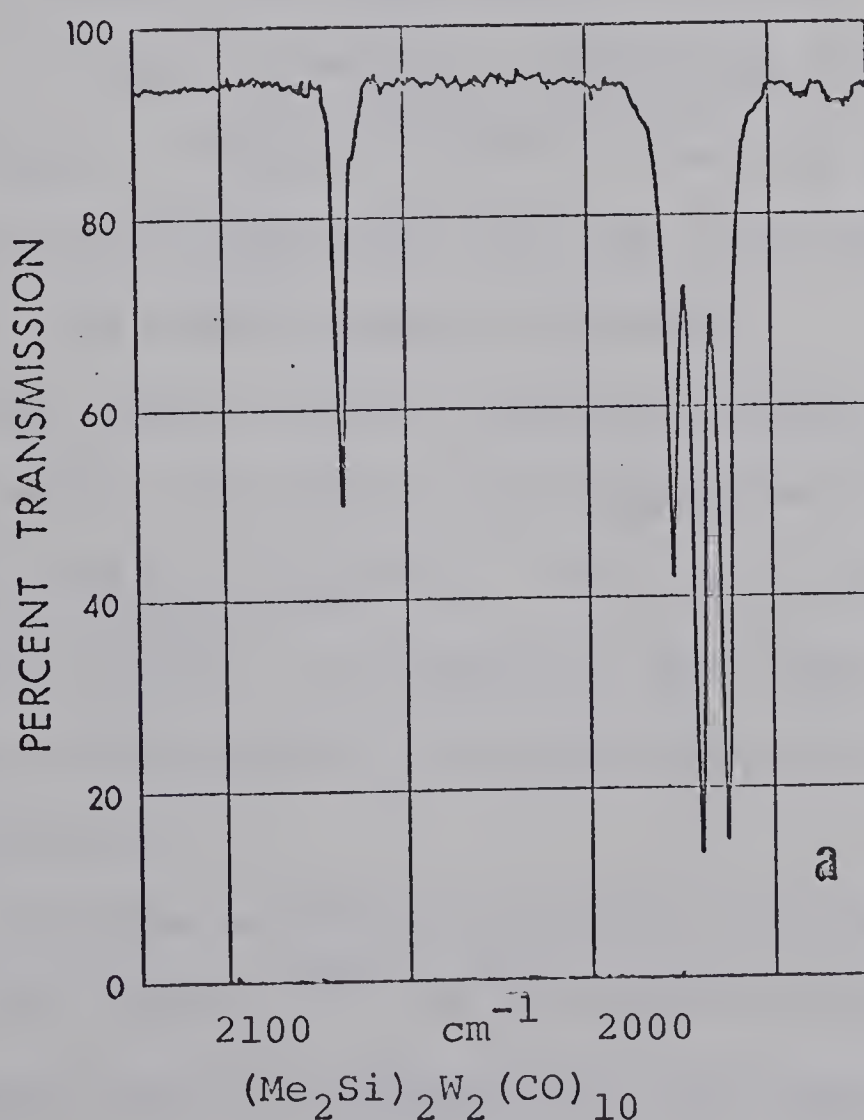


FIGURE 27





Complex  $(R_2Si)_2H_2W_2(CO)_8$

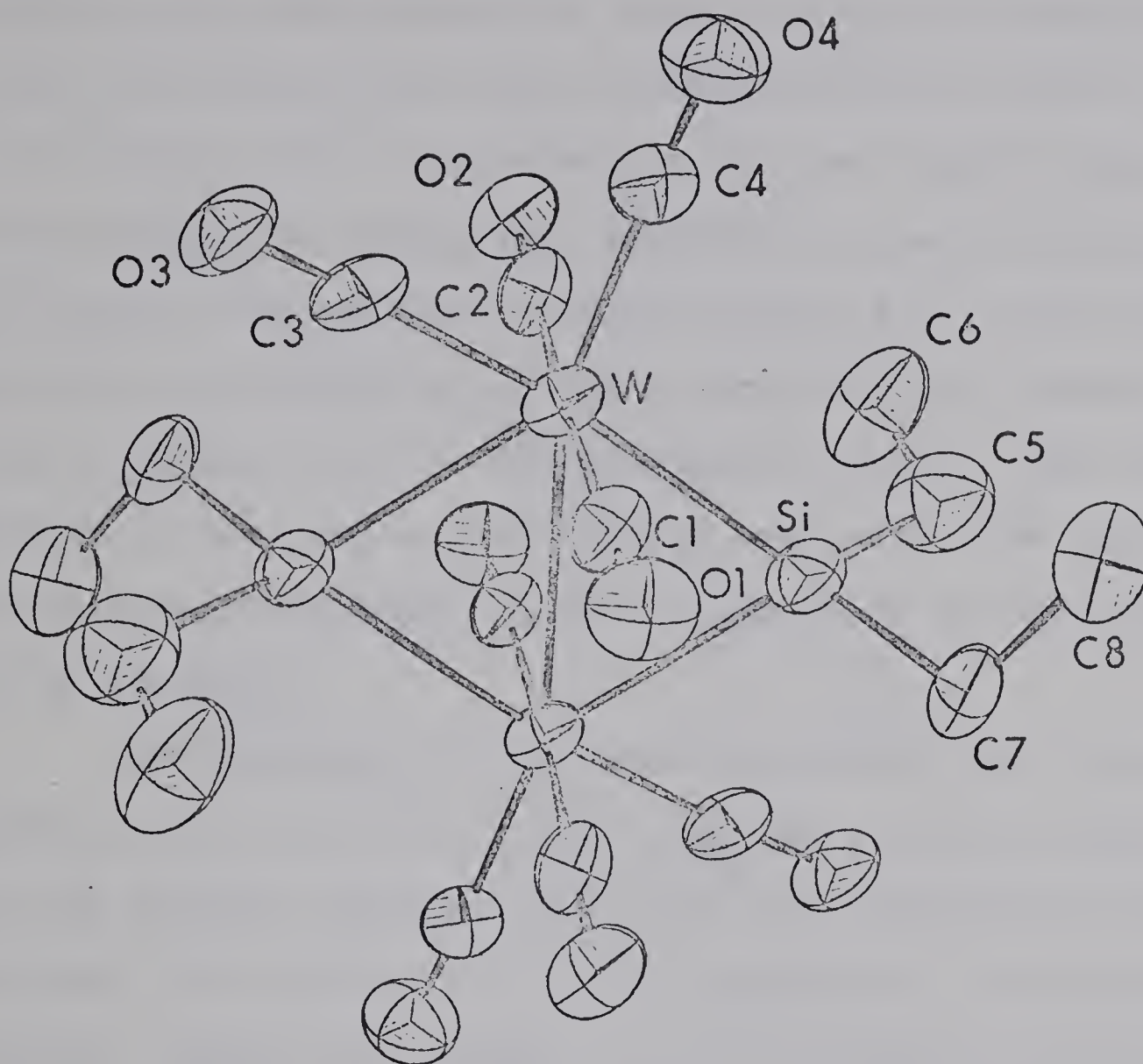
These complexes are yellow, air-stable crystalline solids which are stable and soluble in hexane, benzene, chloroform and dichloromethane. The molybdenum analog  $(Et_2Si)_2H_2Mo_2(CO)_8$  is somewhat less stable, and decomposes slowly in air.

As in the silicon-rhenium hydrides, nmr integration established the number of transition-metal-bonded hydrogens. For the complex  $(Et_2Si)_2H_2W_2(CO)_8$ , the high-field resonance was rather broad due to coupling with the ethyl protons; a pair of satellites due to coupling with  $^{183}W$  (abundance = 14.3%) was observed ( $J = 40$  Hz). This value is similar to values observed in  $HW(CO)_3Cp$  (36.7 Hz)<sup>124</sup> and  $[HW_2(CO)_{10}]^-$  (~42 Hz)<sup>125,126,127</sup> and is presumably due to the short-range coupling, with the long-range satellites hidden under the broad central resonance.

The mass spectra of the complexes  $(R_2Si)_2H_2W_2(CO)_8$  showed the parent ions with no hydrogen loss but all others in the series  $(R_2Si)_2H_2W_2(CO)_n^+$  ( $0 \leq n \leq 7$ ) showed considerable hydrogen loss. A tendency to lose hydrogen in pairs was observed which will be discussed more fully in the mass spectral section.

The structure of  $(Et_2Si)_2H_2W_2(CO)_8$  has been determined by Bennett and Simpson<sup>128</sup> and is shown in Figure 28; the hydride ligands were not located but the stereochemistry of





### Bond Lengths

W-W;	3.18 Å
W-Si'	2.59 Å
W-Si	2.70 Å

### Bond Angles

W-Si-W'	74.0°
Si-W-C4	110°
Si'-W-C3	66.6°

Molecular Structure of  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  <sup>128</sup>

FIGURE 28



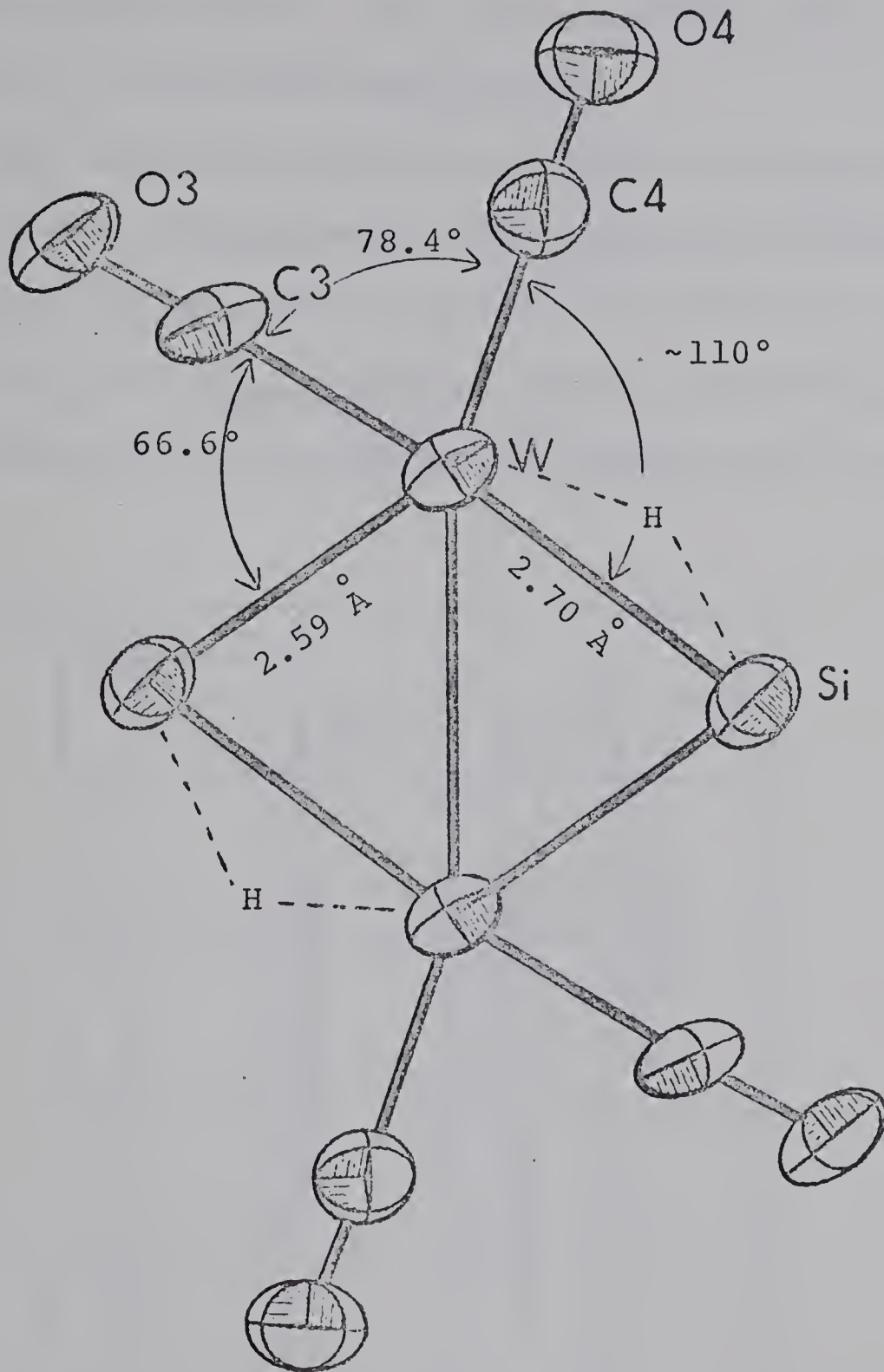
the other ligands suggested the most probable sites. The molecule is centrosymmetric (required crystallographically) with two long and two short tungsten-silicon bonds of  $2.70 \text{ \AA}$  and  $2.59 \text{ \AA}$  respectively. The two hydride ligands are presumed to bridge the two longer tungsten-silicon bonds. The  $\text{W}_2\text{Si}_2$  unit and four carbonyl groups lie in one plane and this projection is shown in Figure 29 (the remaining four carbonyls lie in a perpendicular plane). The carbonyls in this plane are markedly bent away from the longer tungsten-silicon bonds where the hydrogens are presumed to be located.

The presence of two tungsten-silicon bond lengths differing by  $0.11 \text{ \AA}$  in  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  may be contrasted to the rhenium complexes where all rhenium-silicon bond lengths are essentially the same regardless of whether hydride ligands are present or not. In  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  the hydride ligands can possibly be thought of as being partially 'inserted' into the W-Si bonds; it appears that the W-H-Si portion is not linear because structure determinations of some linear M-H-M systems have shown bond lengthenings of ca.  $0.40 \text{ \AA}$ .<sup>105,108</sup> The mass spectrum is also consistent with bent bridges (see the mass spectral discussion). For the complex  $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$ ,<sup>19</sup> where hydrogens are thought to be bent bridges, the two Re-Re bond lengths are  $3.17 \text{ \AA}$  and  $3.03 \text{ \AA}$ .<sup>107</sup>

The tungsten-tungsten distance of  $3.18 \text{ \AA}$  in







Although the hydride ligands were not located, they are shown in the postulated positions.

Planar  $\text{Si}_2\text{W}_2(\text{CO})_4$  Cluster in  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  128

FIGURE 29





$(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  is consistent with a single bond; the acute angle of  $74^\circ$  at the silicon atoms also supports the presence of the metal-metal bond.

The solution infrared spectrum of  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  (Figure 30) is consistent with the solid-state crystal structure; four carbonyl stretching bands are predicted ( $\text{A}_g + 3\text{B}_u$ ) for  $\text{C}_{2h}$  symmetry. Before the X-ray structure was determined, the favored structure was that shown in

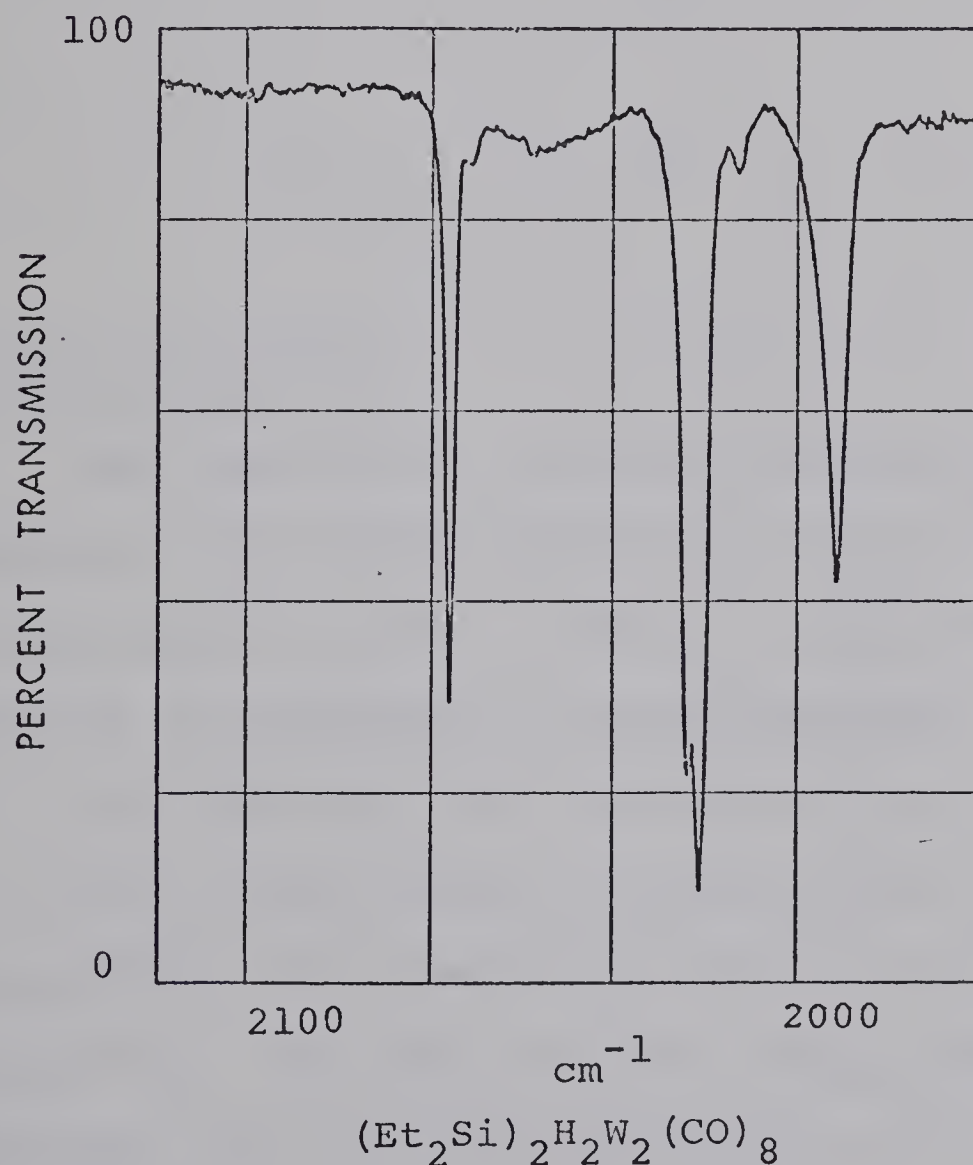
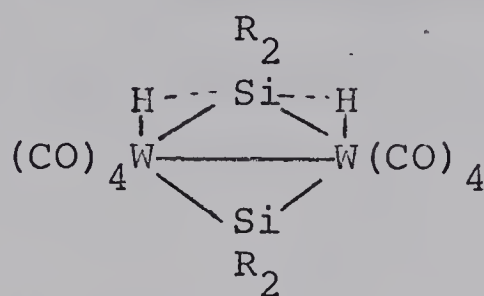


FIGURE 30



33, although in this case a maximum of seven carbonyl bands was predicted. Structure 33 was favored because the precursor to  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  was  $\text{Et}_2\text{SiW}_2(\text{CO})_{10}$ ; this photochemical reaction appeared to be similar to the reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{Et}_2\text{SiH}_2$  to yield  $\text{Et}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ .



33

#### Complex $\text{H}_2\text{Re}_2(\text{CO})_8$

This complex is a yellow, moderately air-stable crystalline solid which decomposes slowly in the light. It is sparingly soluble in hexane or cyclohexane but very soluble in chloroform or dichloromethane.

The hydrogens were detected by nmr (sharp singlet at  $\tau$  19.04) and the number of hydrogens was confirmed by integration of a known molar ratio of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  and  $\text{H}_2\text{Re}_2(\text{CO})_8$ . The mass spectrum of  $\text{H}_2\text{Re}_2(\text{CO})_8$  showed no hydrogen loss from the molecular ion but considerable hydrogen loss in the series  $[\text{H}_2\text{Re}_2(\text{CO})_n]^+$  ( $0 \leq n \leq 7$ ); again a tendency to lose hydrogen atoms in pairs was observed.



The infrared spectrum of  $\text{H}_2\text{Re}_2(\text{CO})_8$  shows four carbonyl stretching bands (Figure 31) consistent with  $D_{2h}$  symmetry as found in the tetracarbonyl halide dimers of manganese and rhenium, 3.<sup>37,38</sup> The X-ray crystal structure of  $\text{H}_2\text{Re}_2(\text{CO})_8$  has been determined by M. J. Bennett and W. Hutcheon (Figure 32)<sup>129</sup> and confirms the proposed  $D_{2h}$  structure. Although the hydrogens were not located, the stereochemistry of the carbonyls was the same as found in  $[\text{BrMn}(\text{CO})_4]_2$ .<sup>38</sup>

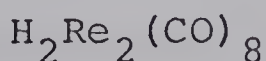
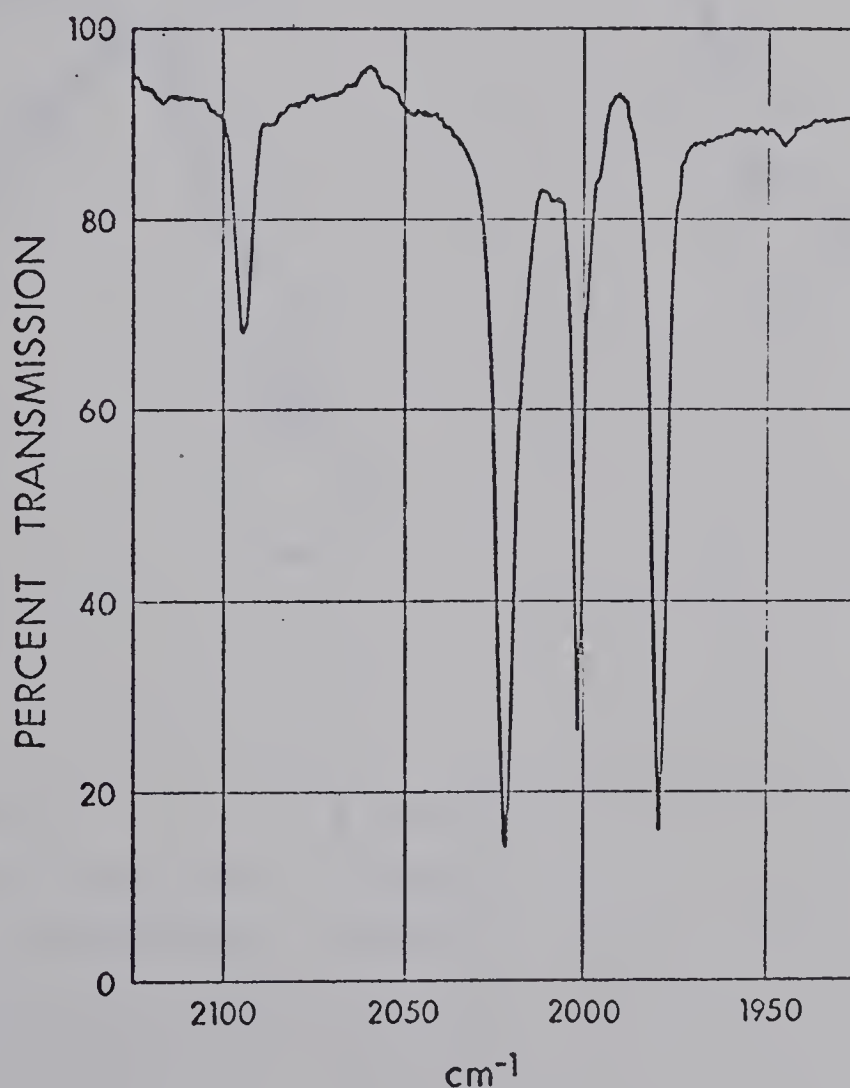
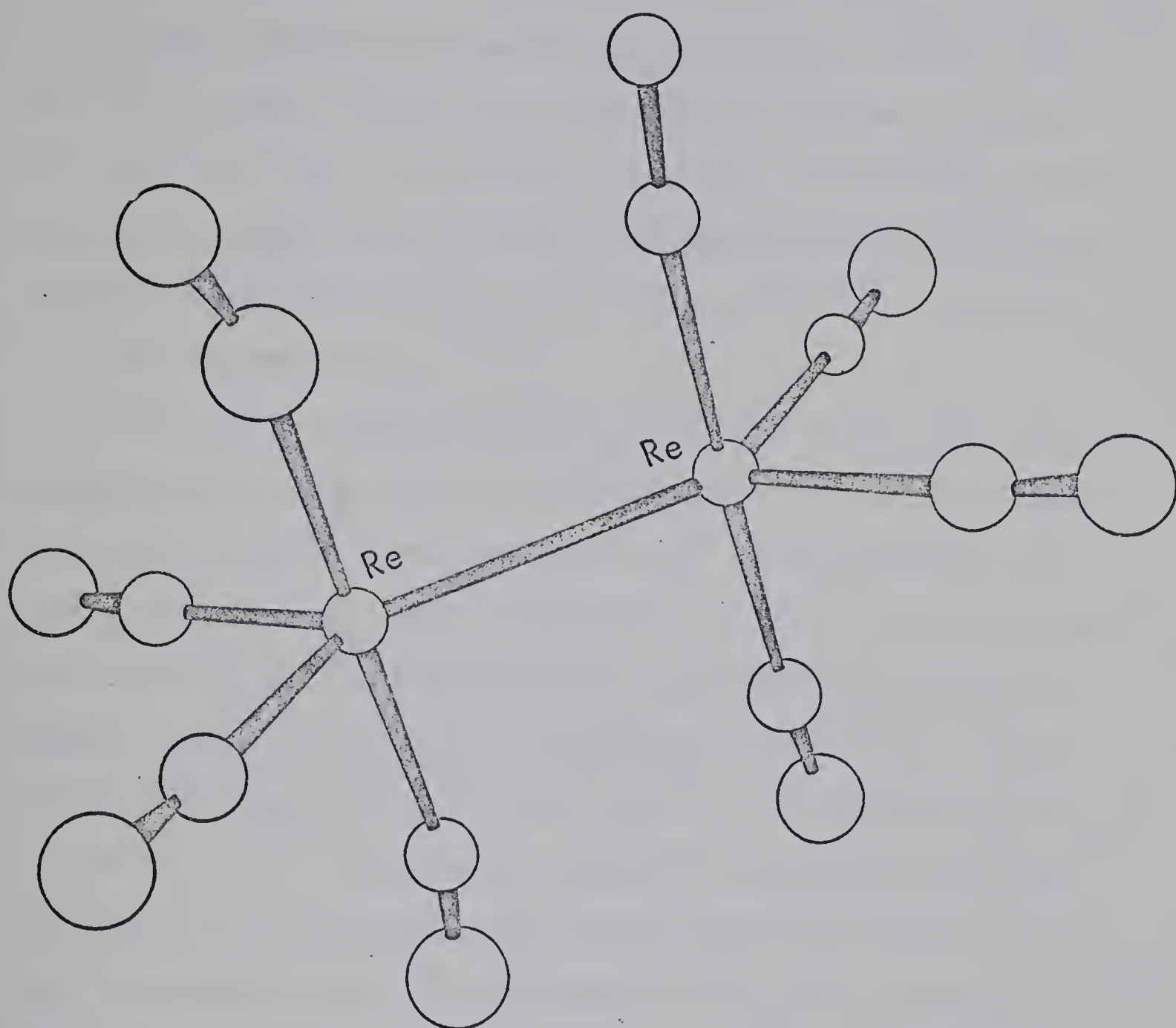


FIGURE 31





Re-Re	2.894	Å
average Re-C(trans CO)	2.015	Å
average Re-C(trans H)	1.919	Å
average C-O(trans CO)	1.11	Å
average C-O(trans H)	1.15	Å

Molecular Structure of  $\text{H}_2\text{Re}_2(\text{CO})_8$  <sup>129</sup>

FIGURE 32





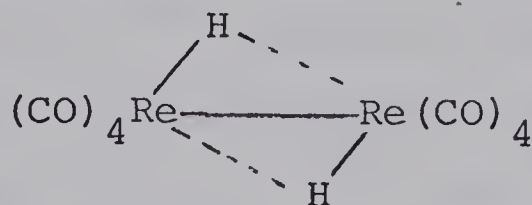
A comparison of the infrared spectra of  $\text{H}_2\text{Re}_2(\text{CO})_8$  and  $\text{D}_2\text{Re}_2(\text{CO})_8$  (prepared from  $\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$ ) in the 2500-800  $\text{cm}^{-1}$  region showed no bands which could be assigned to a Re-H or Re-D stretching frequency. A similar situation has been encountered in other hydrogen-bridged polynuclear rhenium carbonyls such as  $[\text{HRe}(\text{CO})_4]_3$ ,<sup>130,131</sup>  $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^\ominus$ ,<sup>107</sup> and  $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^\ominus$ .<sup>132</sup>

The Raman spectra of  $\text{H}_2\text{Re}_2(\text{CO})_8$  and  $\text{D}_2\text{Re}_2(\text{CO})_8$  have unequivocally located the  $\text{Re} \begin{smallmatrix} \diagup \text{H} \diagdown \end{smallmatrix} \text{Re}$  modes at 1272 and 1382  $\text{cm}^{-1}$  which shift to 924 and 974  $\text{cm}^{-1}$  on deuteration.<sup>115</sup> Other polynuclear rhenium hydrides which have been prepared by Kaesz et al. showed bridging hydrogen modes in the Raman spectra at similar frequencies:  $[\text{HRe}(\text{CO})_4]_3$ , (1100  $\text{cm}^{-1}$ ),<sup>131</sup>  $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^\ominus$  (1100  $\text{cm}^{-1}$ ),<sup>107</sup> and  $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^\ominus$  (1165  $\text{cm}^{-1}$ ).<sup>132</sup> A band at 1000  $\text{cm}^{-1}$  (infrared) has been assigned to the stretching of the hydrogen which bridges two manganese atoms in the compound  $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ , 21.<sup>109</sup> These frequencies, which are well below the 2100-1700  $\text{cm}^{-1}$  region normally associated with terminal metal-hydrogen stretches, strongly indicate hydrogen bridges in these complexes.

The above hydrogen bridges should be distinguished from the silicon-hydrogen-metal interactions suggested previously. In  $\text{H}_2\text{Re}_2(\text{CO})_8$  the hydrogens can be considered to be located in symmetrical bridging positions between the two equivalent rhenium tetracarbonyl moieties (there is

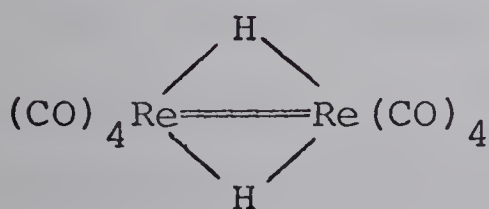


some debate about the exact nature of bridges of this type; the hydrogens may be unsymmetrically located such as in 34).<sup>106,108</sup> For the silicon complexes such as  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ , the suggestion was that the hydrogens are 'normally' bonded to the rheniums with a small bonding interaction with the silicon.

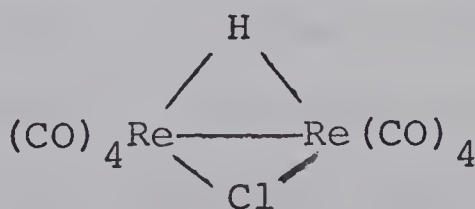


34  
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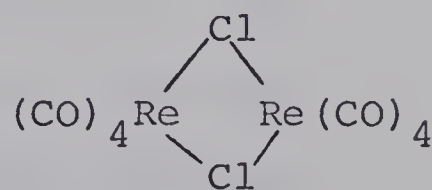
According to the effective atomic number formalism, a rhenium-rhenium double bond would be predicted for the complex  $\text{H}_2\text{Re}_2(\text{CO})_8$  (each rhenium atom would obtain the required eleven electrons in the following manner, eight from the four carbonyls, one from the bridging hydrogens, one half from each bridge, and two from the rhenium-rhenium double bond). Similarly one would predict a single rhenium-rhenium bond and no metal-metal bond for the complexes  $\text{HClRe}_2(\text{CO})_8$  and  $\text{Cl}_2\text{Re}_2(\text{CO})_8$  respectively as shown below.



35  
~~



36  
~~



37  
~~



The observed Re-Re bond length for  $\text{H}_2\text{Re}_2(\text{CO})_8$  is  $2.89 \text{ \AA}$ <sup>129</sup> and does not appear short enough for a double bond when compared to the Re-Re single bond length of  $3.02 \text{ \AA}$  in  $\text{Re}_2(\text{CO})_{10}$ .<sup>40</sup> For some polynuclear metal halides of the third row transition elements, Cotton suggests bond length differences of approximately  $0.30 \text{ \AA}$  between single- and double-bonded species.<sup>155</sup> However, structure determinations of hydrogen-bridged rhenium-rhenium 'single' bonded complexes such as  $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$ <sup>107</sup> and  $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^-$ <sup>132</sup> indicate that these bond lengths are  $3.16 - 3.18 \text{ \AA}$ . Using this range for the Re-Re single bond length, the bond shortening in  $\text{H}_2\text{Re}_2(\text{CO})_8$  would be ca.  $0.29 \text{ \AA}$  and makes the double bond more plausible. The effective atomic number treatment in these cases may be misleading and a more satisfactory result appears to be indicated by a molecular orbital approach.<sup>133</sup> Bond orders for a single hydrogen-bridged species are less than one and less than two for the double-bridged  $\text{H}_2\text{Re}_2(\text{CO})_8$  by this treatment.

#### Complex $\text{HClRe}_2(\text{CO})_8$

This complex is a white, air-stable crystalline solid which is sparingly soluble in hexane or cyclohexane. The proposed  $\text{C}_{2v}$ ,  $\sim\sim$ , structure (this can be derived from the structure of  $\text{H}_2\text{Re}_2(\text{CO})_8$  by replacing one bridging hydrogen with a chlorine) would predict a maximum of seven infrared active carbonyl stretching bands. The infrared spectrum





of  $\text{HClRe}_2(\text{CO})_8$  is shown in Figure 33 exhibiting four bands; this pattern very much resembles the patterns of the tetracarbonyl halide dimers of rhenium and manganese.<sup>37</sup> This suggests that coupling between the two  $\text{Re}(\text{CO})_4$  groups in  $\text{HClRe}_2(\text{CO})_8$  may be negligible. A comparable compound  $\text{H}(\text{PPh}_2)\text{Mn}_2(\text{CO})_8$ , 18, also showed only four carbonyl bands.<sup>135</sup>

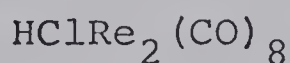
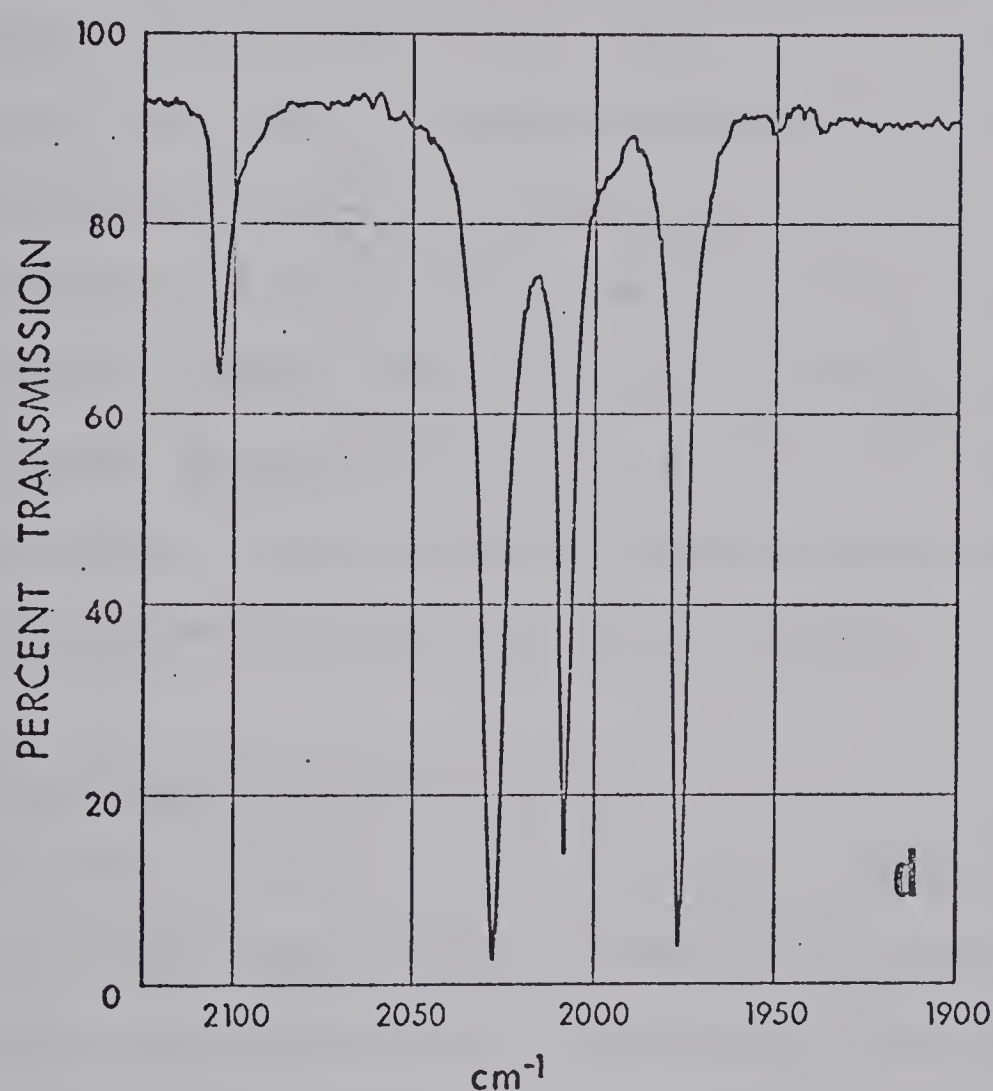


FIGURE 33

Another possible variation in the structure of  $\text{HClRe}_2(\text{CO})_8$  would involve displacement of the hydrogen toward the rhenium-rhenium axis to give a linear  $\text{Re-H-Re}$





bridge such as indicated for  $\text{HMnRe}_2(\text{CO})_{14}$ , <sup>17, 105</sup> or  $[\text{HCr}_2(\text{CO})_{10}]^-$ , <sup>20, 108</sup>. This structure would also have  $C_{2v}$  symmetry but the longer Re-Re distance would mean that coupling between the two  $\text{Re}(\text{CO})_4$  moieties is even more likely to be negligible.

The mass spectrum of  $\text{HClRe}_2(\text{CO})_8$  adds support to the linear Re-H-Re structure. Hydrogen loss is observed in the series  $[\text{HClRe}_2(\text{CO})_n]^+$  only for  $0 \leq n \leq 4$ ; this is similar to  $\text{HRe}_3(\text{CO})_{14}$  for which hydrogen loss is observed in the series  $[\text{HRe}_3(\text{CO})_n]^+$  only for  $0 \leq n \leq 3$ .<sup>136</sup> The mass spectrum of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ , where bent hydrogen bridges are present, showed hydrogen loss occurring throughout the whole series  $[\text{H}_3\text{Re}_3(\text{CO})_n]^+$  ( $0 \leq n \leq 12$ ).<sup>136</sup> The next section gives a more detailed account of the mass spectra of the hydrides discussed in this chapter.

### 3. Mass Spectra and Structure

The mass spectra of the dinuclear transition-metal carbonyls described in this Chapter were used in (a) determining the exact molecular formulae from the isotope patterns and mass numbers and (b) in assessing relationships between fragmentation patterns and structure.

#### Characterization of the Complexes

Mass spectra proved to be a most valuable tool in readily determining the exact molecular formulae of the

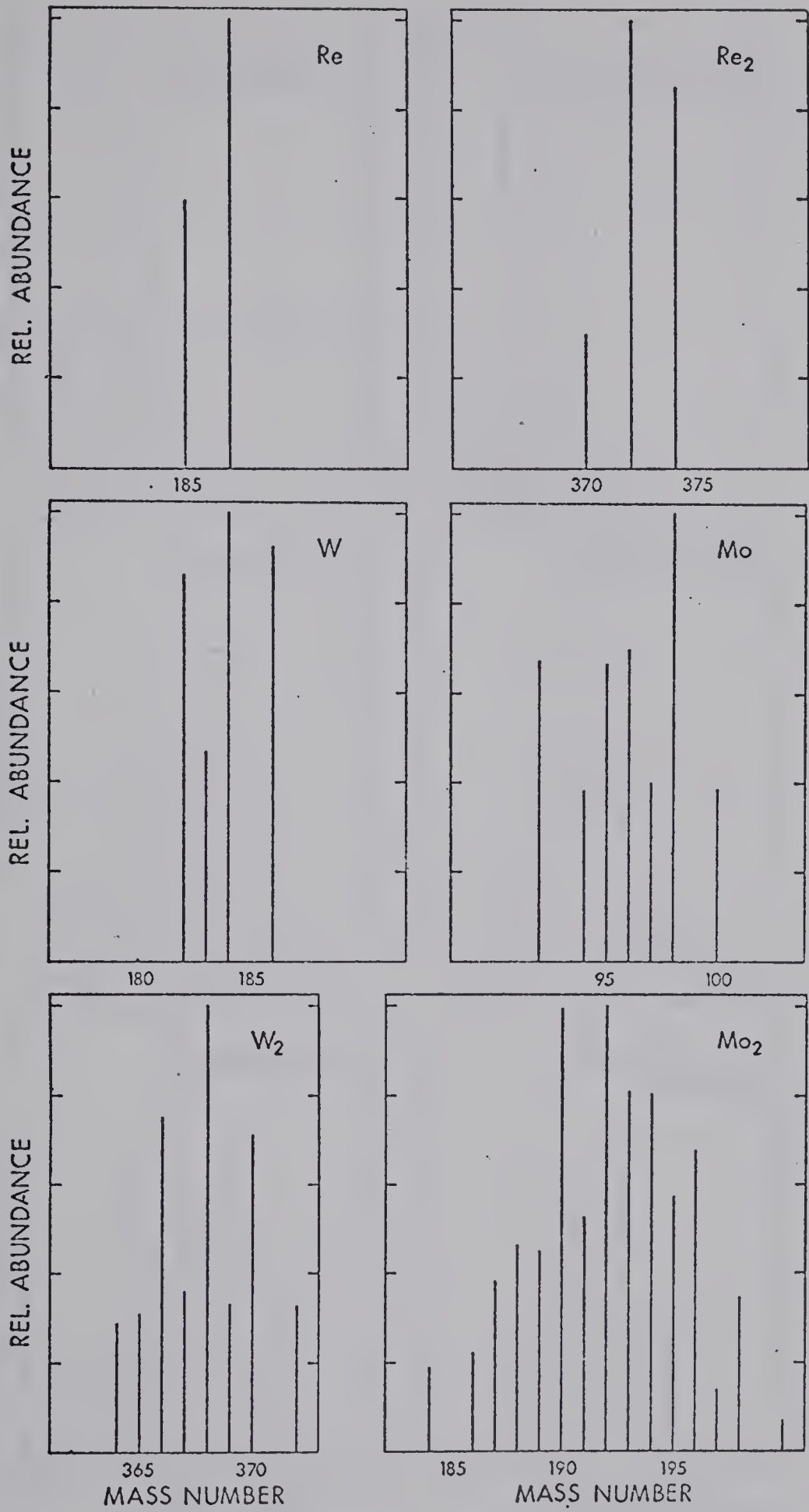


of the hydride complexes described in the previous section. Other techniques such as elemental analysis, nmr and infrared spectra, however, must be used in conjunction with mass spectra because in some cases the molecular ion may not necessarily be observed. The molecular ions were observed for all the compound types just discussed (24-31) except the complexes  $(R_2SiH_2)_2Re_2(CO)_6$ , 25, where the highest fragment observed was  $[(R_2Si)_2H_2Re_2(CO)_6]^+$ .

Since rhenium, tungsten and molybdenum are polyisotopic in their naturally occurring states, characteristic mass spectral isotope patterns are observed for mono- and dinuclear species. Figure 34 shows the expected isotope patterns for the three metals. Similarly the expected pattern for any combination of elements containing polyisotopic elements can be calculated. (The calculated mass spectral patterns and exact masses were obtained using a computer program prepared by Drs. R. S. Gay and E. H. Brooks of this department). Even mainly monoisotopic elements such as carbon and silicon can change the pattern markedly if present in sufficient amounts. This is illustrated by comparing the isotope patterns in Figure 35 with the patterns for the bare metals in Figure 34. Therefore, for such systems, ions can normally be readily identified by comparing calculated and observed patterns without resorting to tedious exact mass measurements.

The calculated and the observed isotope patterns for

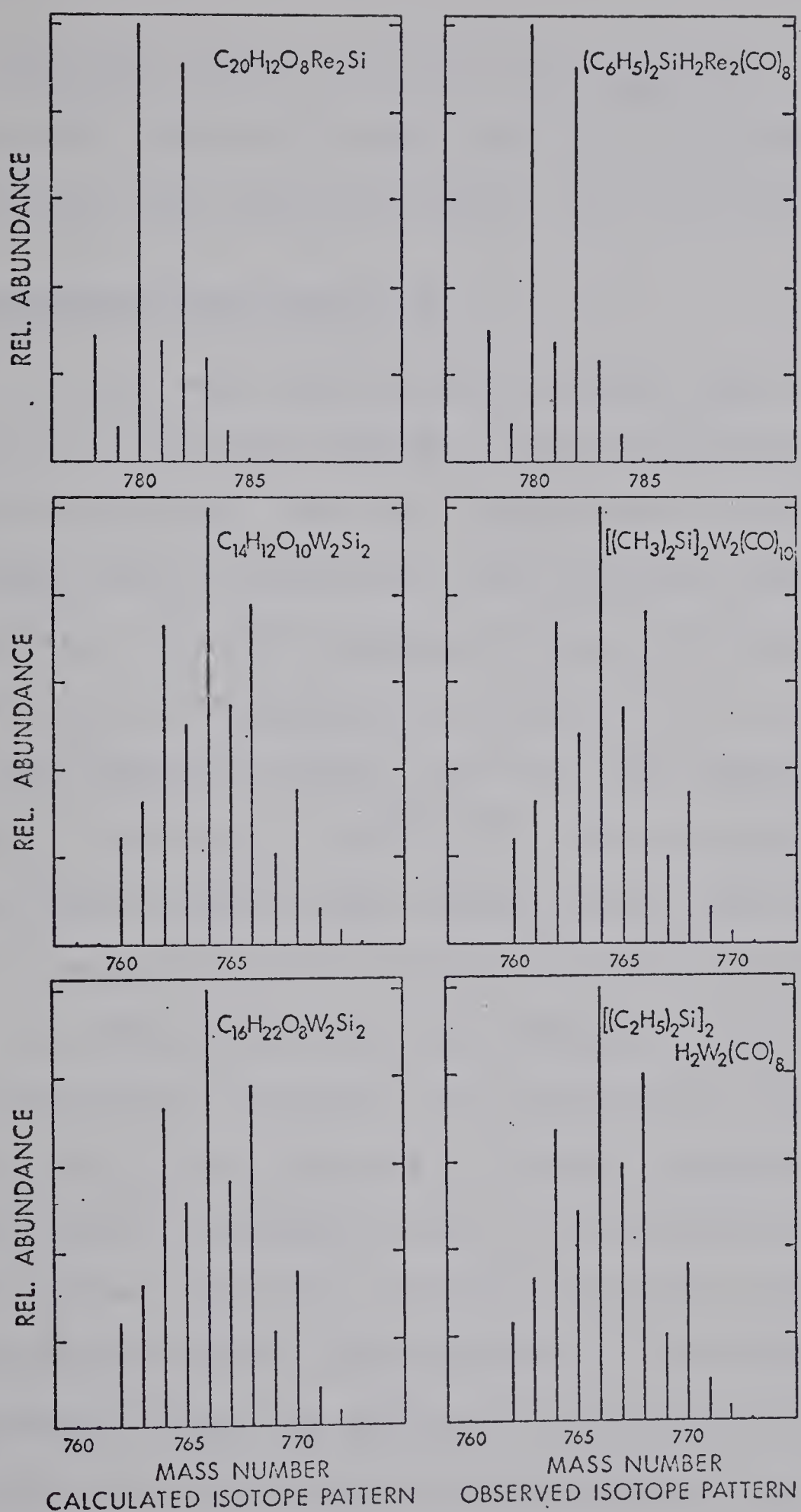




Calculated Mass Spectral Isotope Patterns

FIGURE 34





Calculated and Observed Mass Spectral Isotope Patterns

FIGURE 35





the molecular ions of some of the complexes are shown in Figure 35. As can be seen, very good agreement between calculated and observed patterns was obtained.

### Fragmentation and Structure

It has been shown by many workers that a general feature of the mass spectra of most transition metal carbonyl derivatives (mono and polynuclear) is the presence of peaks which correspond to the stepwise loss of the carbonyls. Thus the compounds  $M(CO)_6$  ( $M = Cr, Mo, W$ ) showed ions corresponding to  $M(CO)_n^+$  for  $0 \leq n \leq 6$ <sup>137</sup> and the compounds  $M_3(CO)_{12}$  ( $M = Fe, Ru$ ) showed the ions  $M_3(CO)_n^+$  for  $0 \leq n \leq 12$ .<sup>138,139</sup> As expected, the compounds described in this Chapter showed ions corresponding to the progressive CO loss from the molecular ions.

In the present work, the fragmentation of the silyl dinuclear metal hydrides, and the hydrides  $H_2Re_2(CO)_8$  and  $HClRe_2(CO)_8$ , were examined in order to obtain information regarding the attachment and/or location of the transition metal bonded hydrogens. All the complexes studied showed fragmentation series corresponding to the stepwise loss of carbonyls from the molecular ions with the number of carbonyls lost being equal to the number in the complex. Also accompanying the CO loss series were peaks corresponding to loss of one or more of the hydride ligands. The competition between hydrogen loss and carbonyl loss may



suggest some structural or bonding features.

Data on hydrogen loss from the molecular ion and its CO loss series for representative compounds of each type are summarized in Table VI. The numbers in the Table give the total percentage of hydridic hydrogen lost for any  $n$ . As examples: (a) for the spectrum of  $\text{HClRe}_2(\text{CO})_8$  with  $n = 2$ , the relative abundances of  $[\text{HClRe}_2(\text{CO})_2]^+$  and  $[\text{ClRe}_2(\text{CO})_2]^+$  are 78 and 22 respectively; (b) for  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  with  $n = 3$ , the relative intensities of  $[\text{Ph}_2\text{SiRe}_2(\text{CO})_3]^+$ ,  $[\text{Ph}_2\text{SiHRe}_2(\text{CO})_3]^+$  and  $[\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_3]^+$  are 70, 10 and 20 respectively, and thus 
$$\frac{70 + \frac{1}{2}(10)}{70+10+20}(100)\% = 75\%.$$
 For some fragments, overlap with other fragments made it impossible even to estimate the hydrogen loss. Because of the absence of overlapping series, more accurate relative intensity data were obtained for  $\text{H}_2\text{Re}_2(\text{CO})_8$  and these are tabulated in Table VII.

It has been shown that in cases so far studied, terminal hydrogens compete more effectively with CO loss than bridged hydrogens. However, in some cases, these differences are very subtle and even very closely related species may differ in their fragmentation patterns. Kaesz *et al.*<sup>136</sup> have found that no hydrogen loss from the molecular ions is observed for the bridged species  $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$  and  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ ; in contrast the terminally bonded  $\text{HMn}(\text{CO})_5$  shows competitive hydrogen and CO loss everywhere in the spectrum.<sup>140</sup> The compound



TABLE VI

TOTAL HYDROGEN LOSS IN MASS SPECTRA OF HYDRIDES <sup>a</sup>

Compound	n								
	0	1	2	3	4	5	6	7	8
$\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	b	78	85	75	95	100	b	100	0
$(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$	c	c	c	c	75	70	60 <sup>d</sup>	-	-
$(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$	e	e	e	e	e	65	60	40 <sup>f</sup>	-
$(\text{Me}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$	e	e	e	100	100	100	100	95	0
$\text{H}_2\text{Re}_2(\text{CO})_8$	83	75	77	78	88	87	86	24	0
$\text{HClRe}_2(\text{CO})_8$	65	28	22	11	5	<1	0	0	0

<sup>a</sup> For each value of n , entries give percent of total "hydridic" hydrogen for all m in  $[(\text{R}_2\text{Si})_{\underline{1}}\text{H}_{\underline{m}}\text{M}_2(\text{CO})_{\underline{n}}]^+$  which appears in peaks at m = 0 or 1 (or m = 0, 1, 2, or 3 in the case of  $(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$ ).

<sup>b</sup> Weak or barely observable, cannot be analyzed.

<sup>c</sup> Obscured by series  $[(\text{MeSi})_2\text{Re}_2(\text{CO})_n]^+$ .

<sup>d</sup> Molecular ion not observed  $[(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_6]^+$  is principal species; see text.

<sup>e</sup> Analysis not possible due to overlap by other fragments.

<sup>f</sup> For ions  $[(\text{Me}_2\text{Si})_2\text{H}_{\underline{m}}\text{Re}_2(\text{CO})_7]^+$  m, intensity: 0, 38 , 1, 4 , 2, 58



TABLE VII

DETAILED HYDROGEN LOSS IN MASS SPECTRUM OF  $\text{H}_2\text{Re}_2(\text{CO})_8^{a,b}$

Ion									
$[\text{H}_2\text{Re}_2(\text{CO})_n]^+$	2	6	7	10	4	8	11	74	100
$[\text{HRe}_2(\text{CO})_n]^+$	30	38	33	25	16	12	5	5	0
$[\text{Re}_2(\text{CO})_n]^+$	68	56	60	65	80	81	84	21	0

a  
 Entries give relative intensities for the three possible  $\underline{m}$  value corresponding to each  $\underline{n}$  in the series  $\text{H}_{\underline{m}}\text{Re}_2(\text{CO})_{\underline{n}}$ .

b  
 Figures in Table VI are calculated from data of this type. Thus total hydrogen loss from  $\text{H}_2\text{Re}_2(\text{CO})_{\underline{n}}$  for  $n = 4$  is 88%.







$\text{H}_3\text{Re}_3(\text{CO})_{12}$ , which is presumed to be isostructural with  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ , shows hydrogen loss competing effectively in all the multiplets.<sup>136</sup>

Lewis et al.<sup>141,142,143</sup> have observed no molecular ion for  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  while  $\text{H}_4\text{Os}_4(\text{CO})_{12}$  shows the molecular ion and no hydrogen loss until four carbonyls have been removed. The highest mass fragment observed in the spectrum of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  was  $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^+$ . On the other hand, molecular ions are observed for both  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  and  $\text{H}_2\text{Os}_4(\text{CO})_{13}$ ; these two complexes show no hydrogen loss until several carbonyls have been lost. From other spectroscopic evidence all of the above ruthenium and osmium complexes are postulated to have bridging hydrogens.

Recently from this laboratory Moss and Graham<sup>144, 145,146</sup> have reported the mass spectra of the polynuclear osmium carbonyl hydrides  $\text{H}_2[\text{Os}(\text{CO})_4]_n$  ( $n = 2, 3, 4$ ). The hydrogens in these complexes are most likely terminal. By comparing the mass spectra of these complexes with the spectrum of the bridged species  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ,<sup>147</sup> Graham and Moss<sup>146</sup> conclude that for polynuclear carbonyl hydrides it is very difficult to differentiate between bridging and terminal hydrogens merely on the basis of mass spectral data.

In the present work, four of the complexes (from Table VI) show no hydrogen loss from the molecular ion:



$\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ ,  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$ ,  $\text{H}_2\text{Re}_2(\text{CO})_8$  and  $\text{HClRe}_2(\text{CO})_8$ . This is consistent with hydrogen bridges in these species. The properties and structures of complexes of the types  $(\text{R}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  and  $(\text{R}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  are known to be closely related to the complexes  $\text{R}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ ; yet the former two complexes show considerable hydrogen loss from the molecular ions (Table VI). It is apparent that a sharp distinction as to the character of hydrogen in these compounds cannot be made solely on the basis of whether there is hydrogen loss from the molecular ion.

As noted previously, the molecular ion was not observed for  $(\text{R}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$ ; the highest mass fragment observed was  $[(\text{R}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_6]^+$ , i.e. the molecular ion minus two hydrogens. This is similar to the mass spectrum of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ <sup>143</sup> where the highest fragment observed was  $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^+$ . The relative intensities of fragments of the series  $[(\text{Me}_2\text{Si})_2\text{H}_m\text{Re}_2(\text{CO})_6]^+$  are zero for  $m = 4$ , zero for  $m = 3$ , 80 for  $m = 2$ , zero for  $m = 1$  and 16 for  $m = 0$ . This tendency for hydrogen atoms to fragment in pairs is characteristic of all the silyl-metal hydrides and of  $\text{H}_2\text{Re}_2(\text{CO})_8$  (Table VII). This preference for simultaneous loss of two hydrogens has also been observed for  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ ,<sup>141</sup>  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ ,<sup>141</sup> and  $\text{H}_2[\text{Os}(\text{CO})_4]_n$ .<sup>146</sup>

In the mass spectrum of  $\text{HClRe}_2(\text{CO})_8$ , hydrogen loss occurs only after the loss of four carbonyls (Table VI). Furthermore, hydrogen loss for  $n = 1, 2, 3, 4$  is not as pro-



nounced as in the silyl-metal hydrides (Table VI). This mass spectral behaviour seems characteristic of linear Re-H-Re bridges as found in  $\text{HRe}_3(\text{CO})_{14}$  and  $\text{HMnRe}_2(\text{CO})_{14}$ .<sup>136, 105, 108</sup> The mass spectra of these and other complexes which are postulated to have similar linear bridges are discussed in detail in the next Chapter. A possible linear Re-H-Re system in  $\text{HClRe}_2(\text{CO})_8$  has previously been suggested.

One common feature of the mass spectra of the silyl-metal hydrides in Table VI is that the intensity of  $[\text{R}_2\text{SiH}]^+$  is invariably five to ten times more intense than that of  $[\text{R}_2\text{Si}]^+$ . Spectra of the non-hydride complexes  $[\text{R}_2\text{SiRe}(\text{CO})_4]_2$  in the same regions show only  $[\text{R}_2\text{Si}]^+$ . This circumstance is at least consistent with the hydride ligands located proximate to the silicons. The ion  $[\text{R}_2\text{SiH}_2]^+$  is not observed for any of the hydride complexes.

In summary, mass spectrometry is an indispensable tool in the characterization of the hydride complexes, and does permit some structural inferences. However, other supporting data must be used to provide more convincing evidence for the proposed structural features.

#### 4. Summary and Conclusions

The spectral data and the X-ray structure determinations intimate that hydrogen 'bridges' (M-H---Si) may be present in the silyl dinuclear metal hydrides; for the complexes  $\text{H}_2\text{Re}_2(\text{CO})_8$  and  $\text{HClRe}_2(\text{CO})_8$ , it appears clear that





the hydrogens are bridging. For the silicon compounds, the most that is suggested is a weak bonding interaction between the hydrogen and silicon, while essentially retaining a normal covalent transition-metal to hydrogen bond. The spectral properties of the silicon-metal hydrides can be compared to the properties of compounds in which hydrogen bridges occur between boron and a transition metal.

Summing the spectral and structural aspects of  $\text{H}_2\text{Re}_2(\text{CO})_8$  and  $\text{HClRe}_2(\text{CO})_8$ , one can logically conclude that the hydrogens are located in bridging positions between the rhenium atoms. The high field nmr resonances for both complexes appear at higher  $\tau$  values than for the terminally bonded  $\text{HRe}(\text{CO})_5$  and this is indicative of a bridging hydrogen as has been pointed out.<sup>143</sup> Although the hydrogens were not located, the X-ray structure of  $\text{H}_2\text{Re}_2(\text{CO})_8$  shows that the heavy atom framework is consistent with the  $D_{2h}$  structure as is the carbonyl stretching band pattern in the infrared spectrum. The carbonyl stretching pattern of  $\text{HClRe}_2(\text{CO})_8$  is similar and implies a similar arrangement of heavy atoms. The mass spectral implications of hydrogen bridges for these two complexes has just been discussed in the previous section. Probably the most convincing evidence for bridged hydrogens is the frequency of the hydride 'stretch' at ca.  $1300\text{ cm}^{-1}$  (Raman) for  $\text{H}_2\text{Re}_2(\text{CO})_8$ . As mentioned previously, other rhenium and manganese complexes with hydrogen bridges were found to show hydrogen modes in





the  $1000 - 1200 \text{ cm}^{-1}$  region. Recently a double hydrogen bridge has been proposed for  $[(\text{C}_{10}\text{H}_{10})\text{Ti}]_2$  and the infrared frequency at  $1230 \text{ cm}^{-1}$  has been assigned to the bridging hydrogen mode.<sup>148</sup> Terminal transition metal-hydrogen stretches are found in the  $1700 - 2100 \text{ cm}^{-1}$  region.

The effective atomic number formalism can accomodate either terminal or bridged hydrogens for the silicon-metal hydrides reported here. For example in  $\text{R}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  terminal Re-H bonds would mean that each  $\text{Re}(\text{CO})_4$  moiety acquires the needed three electrons from a Re-Re bond, a Si-Re bond and a Re-H bond. In a bridged system, the Si-H-Re part could be regarded as a three-centre two electron bond in which both electrons originate in the original Si-H bond. It would even be possible to consider the Si-H bond as a two-electron donor to rhenium. A suggestion of this type has recently been made in connection with kinetic studies on  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$ .<sup>151</sup>

As noted at the beginning of this Chapter, the occurrence of hydrogen in a definite bridging position between a main group element and a transition metal was known only for boron. Some of the spectroscopic and structural features of these boron complexes can be summarized. X-ray structure determinations of  $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ ,<sup>109</sup>  $(\text{PPh}_3)_2\text{CuBH}_4$ ,<sup>110</sup> and  $\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8$ ,<sup>111</sup> have substantiated the existence of three-centre metal-hydrogen-boron bridging systems. High-field nmr resonances



were observed for  $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$  ( $\tau$  29)<sup>109</sup> and  $\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8$  ( $\tau$  17.3).<sup>111</sup> From the data available, the hydrogen mode in the M-H-B system appears to lie in the 2000-2200  $\text{cm}^{-1}$  region (infrared active)<sup>109,111,149</sup> which can be compared to the terminal B-H region of 2400-2600  $\text{cm}^{-1}$ .<sup>109</sup> Thus, it would be difficult to distinguish terminal M-H or bridging M-H-B systems on infrared frequencies alone. Since terminal silicon-hydrogen stretching frequencies are found in the 2050-2250  $\text{cm}^{-1}$  region, it would not be unreasonable if the hydrogen mode of a bridging system such as M-H---Si occurred in the 1700-2000  $\text{cm}^{-1}$  region.

From the data now available for the silyl-metal hydrides, there does not appear to be conclusive evidence for bridged M-H--Si systems. The X-ray structure determinations did not locate the hydride ligands because of the presence of the heavy atoms rhenium and tungsten. However, from the arrangement of the other atoms, the most probable general locations were suggested as discussed for the various complex types. Only small changes in the angles M-M-H can make the silicon-hydrogen distance non-bonding or bonding; structures resulting from these variations in angles will be consistent with the infrared and nmr spectra. The hydride nmr resonances were found at higher field than the terminally bonded compounds such as  $\text{HRe}(\text{CO})_5$  and



$\text{HW}(\text{CO})_3\text{Cp}$ ; this is consistent with bridging hydrogens. However, comparisons like this must be made very carefully because the  $\tau$  values of all silicon-metal hydrides are higher than 'normal'. The mass spectra just discussed in the previous section were shown to be at least consistent with hydrogen bridges.

Because of their absence in the infrared spectra, only a few hydride stretching frequencies have been obtained (by Raman spectroscopy) for the silyl-metal hydrides. These frequencies were found to be in the region normally associated with terminal stretches. Comparable bridging frequencies are not available but the data on the boron complexes suggested that even a bridged  $\text{M-H--Si}$  system may have hydrogen modes in the 'terminal' region as discussed above. In this regard, the mononuclear complex  $\text{Ph}_3\text{SiMnH}(\text{CO})_2\text{Cp}$  shows an Mn-H frequency at  $1900\text{ cm}^{-1}$  in the Raman spectrum;<sup>115</sup> the solid-state crystal structure determination of this compound has unambiguously located the hydride ligand in a bridging position.<sup>129</sup> The synthesis and properties of  $\text{Ph}_3\text{SiMnH}(\text{CO})_2\text{Cp}$  will be described in Chapter V.

A characteristic feature of the silyl dinuclear metal hydrides described in this Chapter and of  $\text{Ph}_3\text{SiMnH}(\text{CO})_2\text{Cp}$  is the lack of an observable metal-hydrogen stretching mode in the infrared spectra. A recent structure determination of cis- $\text{Ph}_3\text{SiFeH}(\text{CO})_4$ <sup>150</sup> showed the





hydride ligand located at a normal non-bonded distance from the silicon; this compound also lacks a distinct metal-hydrogen stretch in the infrared spectrum.<sup>60</sup> At present it is not clear why these modes are infrared 'inactive' and what, if any, relation this has to the bridging nature of the hydrogens.

Metals of the first transition series such as manganese and chromium do not appear to form isolable analogs of rhenium and tungsten. Therefore, it appears that a neutron diffraction study on complexes such as  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  or  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  may be helpful in establishing the exact location of the hydride ligands.





EXPERIMENTAL SECTIONGeneral procedure and apparatus.

A nitrogen atmosphere was maintained during all reactions, and during work-up procedures by the use of Schlenk apparatus. Small scale irradiations were carried out using a Hanovia Utility Lamp (Model 30620, 140 watts) at a distance of about 10 cm from a quartz flask containing the reaction mixture; the solution was maintained below room temperature during irradiation by means of a water-cooled cold finger. For large-scale irradiations, a Hanovia lamp (No. L679A, 450 watts) was used inside a water-cooled quartz jacket with the solution in the annular space outside the jacket. Reactions using dimethylsilane (bp  $-19^{\circ}$ ) were carried out in Pyrex Carius tubes (approximate volume 70 ml) equipped with a threaded Teflon valve (Fischer and Porter Co.) for intermittent pressure release; work-up procedures for the dimethylsilane reactions were the same as for reactions carried out at atmospheric pressure.

Melting points, microanalyses, infrared and nmr spectra were obtained as previously described. Melting points and microanalytical results are given in Table IX; tabulated infrared carbonyl stretching bands appear in Table X; nmr results are summarized in Table VIII.

Mass spectra were obtained using Associated Electrical Industries MS-9 and MS-12 instruments. Samples were intro-



TABLE VIII

NUCLEAR MAGNETIC RESONANCE DATA FOR THE DINUCLEAR HYDRIDES  
OF RHENIUM, TUNGSTEN AND MOLYBDENUM

<u>Compound</u>	<u><math>\tau</math> for High-field Protons</u>	
$\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	19.56	$(\text{CCl}_4)^a$
$\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	20.56	$(\text{CCl}_4)^b$
$\text{Et}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	20.80	$(\text{CCl}_4)^c$
$(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$	20.01	$(\text{CCl}_4)$
$(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$	20.12	$(\text{CDCl}_3)^d$
$(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$	20.11	$(\text{CCl}_4)^e$
$(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$	20.25	$(\text{CDCl}_3)^d$
$(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$	19.19	$(\text{C}_6\text{H}_6)^d$
$(\text{Et}_2\text{Si})_2\text{H}_2\text{Mo}_2(\text{CO})_8$	18.02	$(\text{C}_6\text{H}_6)^d$
$\text{H}_2\text{Re}_2(\text{CO})_8$	19.04	$(\text{CDCl}_3)$
$\text{HClRe}_2(\text{CO})_8$	22.65	$(\text{CDCl}_3)$

a Phenyl region complex multiplet.

b Methyl resonance 1:2:1 triplet,  $J(\text{CH}_3\text{-H}) = 1.5 \text{ Hz.}$

c Ethyl region complex,  $\text{A}_4\text{B}_6\text{X}_2$  type.

d Ethyl region complex multiplet.

e  $\tau(\text{CH}_3) = 8.70$ ; see Figure 24 and text.



TABLE IX

MELTING POINTS, COLORS AND ANALYTICAL RESULTS OF SILICON-BRIDGED METAL HYDRIDES AND

## RELATED COMPOUNDS

Compound	Mp	Color	Calculated %				Found %			
			C	H	Other		C	H	Other	
$\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	168-169	white	30.77	1.44	Si, 3.60		30.67	1.77	Si, 3.68	
$\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$	160-163	white	30.75	1.80	-		30.72	1.81	-	
$\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	>115 dec	pale-yellow	18.29	1.23	Si, 4.28		18.41	1.33	Si, 4.45	
$\text{Et}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$	> 96 dec	pale-yellow	21.05	1.77	-		21.33	1.95	-	
$(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$	98-100	white	19.23	2.05	-		19.39	2.11	-	
$(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$	63-65	white	24.26	2.99	-		24.03	3.15	-	
$(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$	>130 dec	white	18.18	2.44	-		18.55	2.61	-	
$(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$	>118 dec	white	23.46	3.38	-		23.31	3.52	-	
$\text{H}_2\text{Re}_2(\text{CO})_8$	>115 dec	yellow	16.06	0.34	O, 21.39		16.17	0.45	O, 21.50	
$\text{HClRe}_2(\text{CO})_8$	148-150 dec	white	15.18	0.16	Cl, 5.60		15.16	0.03	Cl, 5.77	
$\text{Ph}_2\text{SiW}_2(\text{CO})_{10}$	120-123 dec	orange	31.82	1.21	Si, 3.38		32.11	1.29	Si, 3.48	

continued.....



TABLE IX (continued)

$\text{Me}_2\text{SiW}_2(\text{CO})_{10}$	>110 dec	orange	20.41	0.86	-	20.89	1.05	-
$(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$	132-135 dec	yellow	25.08	2.90	Si, 7.33	25.16	3.08	Si, 7.51
$(\text{Et}_2\text{Si})_2\text{H}_2\text{Mo}_2(\text{CO})_8$	112-116 dec	yellow	32.56	3.76	Si, 9.52	32.50	3.33	Si, 9.62
$(\text{Me}_2\text{Si})_2\text{W}_2(\text{CO})_{10}$	>150 dec	pale- yellow	22.01	1.58	Si, 7.35	21.90	1.70	Si, 7.81
$[\text{Ph}_4\text{As}]_2^+[(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_6]^-$	>175 dec	orange	50.24	4.22	-	50.06	3.98	-





TABLE X

## INFRARED CARBONYL STRETCHING FREQUENCIES OF SILICON-BRIDGED METAL-CARBONYL HYDRIDES AND

## RELATED COMPOUNDS

Compound	Frequencies <sup>a</sup> cm <sup>-1</sup>		
Ph <sub>2</sub> SiH <sub>2</sub> Re <sub>2</sub> (CO) <sub>8</sub>	2110 (3.2) 2000 (7.2)	2075 (6.7) 1995 (4.5)	2021 (7.7) 1977 (7.4) 2015 (10.0)
Ph <sub>2</sub> SiD <sub>2</sub> Re <sub>2</sub> (CO) <sub>8</sub>	2110 (3.0) 1998 (7.9)	2075 (6.4) 1995 (5.2)	2018 (7.0 sh) 1975 (7.4) 2016 (10.0)
Me <sub>2</sub> SiH <sub>2</sub> Re <sub>2</sub> (CO) <sub>8</sub>	2109 (2.3) 1998 (5.9)	2072 (6.6) 1978 (6.9)	2021 (6.9) 2010 (10.0)
Et <sub>2</sub> SiH <sub>2</sub> Re <sub>2</sub> (CO) <sub>8</sub>	2108 (2.9) 1996 (6.3)	2070 (7.3) 1977 (7.2)	2019 (6.9) 2008 (10.0)
(Me <sub>2</sub> Si) <sub>2</sub> H <sub>2</sub> Re <sub>2</sub> (CO) <sub>7</sub>	2058 (4.6) 1961 (1.2)	1995 (10.0)	1981 (7.0) 1976 (4.2)
(Et <sub>2</sub> Si) <sub>2</sub> H <sub>2</sub> Re <sub>2</sub> (CO) <sub>7</sub>	2057 (6.7) 1959 (1.9)	1994 (10.0)	1981 (8.5) 1977 (5.7)
(Me <sub>2</sub> SiH <sub>2</sub> ) <sub>2</sub> Re <sub>2</sub> (CO) <sub>6</sub>	2057 (6.0)	2049 (0.6)	1993 (7.5) 1987 (10.0)
(Et <sub>2</sub> SiH <sub>2</sub> ) <sub>2</sub> Re <sub>2</sub> (CO) <sub>6</sub>	2055 (5.9) 1974 (1.0)	2047 (0.3)	1991 (7.0) 1984 (10.0)
H <sub>2</sub> Re <sub>2</sub> (CO) <sub>8</sub>	2093 (3.5)	2020 (10.0)	2000 (8.6) 1979 (9.8)
HClRe <sub>2</sub> (CO) <sub>8</sub>	2104 (1.9)	2027 (10.0)	2008 (7.7) 1975 (10.0)
Ph <sub>2</sub> SiW <sub>2</sub> (CO) <sub>10</sub>	2097 (2.9) 1989 (10.0)	2058 (7.0) 1976 (8.3)	2017 (3.7) 1963 (7.9) 2001 (1.6) 1947 (2.2)

continued.....



TABLE X (continued)

$\text{Me}_2\text{SiW}_2(\text{CO})_{10}$	2098(3.5) 1987(8.9) 1939(3.7)	2056(8.8) 1978(10.0)	2019(4.4) 1959(6.8)	2002(4.4) 1952(7.0)
$\text{Et}_2\text{SiW}_2(\text{CO})_{10}$ <sup>b</sup>	2097(3.1) 1985(8.2) 1940(2.0)	2055(8.0) 1976(10.0)	2016(3.2) 1959(6.0)	2000(3.3) 1951(5.0)
$\text{Ph}_2\text{SiMo}_2(\text{CO})_{10}$ <sup>b</sup>	2096(3.0) 1955(8.6) 1952(3.0)	2058(7.5) 1980(10.0)	2023(4.3) 1969(6.5)	2011(4.0) 1964(6.0)
$(\text{Me}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$ <sup>b</sup>	2046(5.7) 1967(0.9)	2039(0.4) 1939(5.1)	1980(8.4 sh)	1978(10.0)
$(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$	2044(8.1) 1964(1.2)	2038(1.2) 1937(6.8)	1977(8.8)	1974(10.0)
$(\text{Et}_2\text{Si})_2\text{H}_2\text{Mo}(\text{CO})_8$	2046(7.9) 1979(0.9)	2039(0.8) 1941(6.3)	1975(8.8)	1982(10.0)
$(\text{Me}_2\text{Si})_2\text{W}_2(\text{CO})_{10}$	2067(4.7)	1975(5.7)	1968(10.0)	1960(9.6)
$[\text{Ph}_4\text{As}]_2^+[(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_6]^{=\text{C}}$	1993(10.0)	1896(9.5)	1880(9.4)	

<sup>a</sup> Cyclohexane solutions. Figures in parentheses are relative band heights on a transmittance scale; sh = shoulder, br = broad.

<sup>b</sup> Characterized only by mass spectrometry and infrared; insufficient quantity for microanalysis and nmr.

<sup>c</sup> In dichloromethane.



duced by direct evaporation of the solid samples at temperatures just sufficient to produce the spectrum (ionizing potential 70 ev). Mass spectra were interpreted with the aid of a computer program which calculated exact masses and isotope combination patterns. This program was written in this department by Drs. E. H. Brooks and R. S. Gay and was based on the algorithm described by Carrick and Glockling.<sup>152</sup> Using these computed patterns the extent of hydrogen loss was assessed by assuming that the observed peak heights represented the sums of the isotope abundance patterns which contributed to the particular pattern. Some of the hydrogen loss abundances in Tables VI and VII were obtained using a least squares computer program prepared by Dr. A. S. Foust in this department.

### Materials

Samples of  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$  and  $\text{Re}_2(\text{CO})_{10}$  were purchased from Pressure Chemical Co., Pittsburgh, Pa. The hexacarbonyls were sublimed before use. Silanes were purchased from Pierce Chemical Co., Rockford, Illinois. A published procedure was used for the preparation of  $\text{Ph}_2\text{SiD}_2$  from  $\text{LiAlD}_4$  and  $\text{Ph}_2\text{SiCl}_2$ .<sup>153</sup> Silicic acid (Mallinckrodt AR 100 mesh) or Florisil (Fisher 100-200 mesh) was used in the chromatography columns. Solvents were of reagent grade which were saturated with dry nitrogen prior to use.





Procedures $\mu$ -Diphenylsilicon-bis(hydridotetracarbonylrhenium),

A magnetically stirred benzene solution (50 ml) of rhenium carbonyl (3.38 g, 5.2 mmol) and diphenylsilane (1.0 g, 5.4 mol) was irradiated with the 140 watt source for 76 hours (irradiation with the 450 watt source for periods from 0.5 - 1.0 hours gave much decomposition and work-up was difficult). Solvent was evaporated at reduced pressure and residual material was sublimed at 60° in high vacuum to remove starting materials. Two recrystallizations from n-hexane at -20° afforded white crystals of the product (1.55 g, 40%).

Complexes  $\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$ ,  $\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ ,  $\text{Et}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ .

These complexes were prepared in a similar fashion to that described above for  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ . Again optimum results were obtained using the smaller 140 watt ultraviolet source. With dimethylsilane and diethylsilane, 50 hours irradiation gave the best yields (35-40%) of the products (for the dimethylsilane reaction the reaction tube was cooled to liquid nitrogen temperature and CO was pumped every five hours). Work-up procedures were the same as for  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ . The preparation of  $\text{Ph}_2\text{SiD}_2\text{Re}_2(\text{CO})_8$  was identical to that of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ ; the mass spectrum





confirmed that deuteration in the compound was greater than 95%. Quantities used were similar to the above procedure for  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ .

Di- $\mu$ -diethylsilicon-bis(dihydridotricarbonylrhenium),  
 $(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$

Six hours' irradiation (450 watt source) of rhenium carbonyl (2.20 g, 3.4 mmol) and diethylsilane (3.0 ml, 25 mmol) in cyclohexane gave a dark-red solution. Monitoring by infrared spectroscopy indicated that  $\text{Et}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  was formed initially and that it was converted on further irradiation to the product. The red solution was evaporated at reduced pressure and the residual dark oil was stirred for 2 hours in a chloroform-silicic acid slurry. Any remaining  $\text{Et}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  was thereby converted to the more easily separated  $\text{H}_2\text{Re}_2(\text{CO})_8$ . This mixture was filtered and chloroform was removed at reduced pressure. The residue was chromatographed on silicic acid (chloroform elution), collecting the main pale-yellow band. Two recrystallizations from n-hexane ( $-20^\circ$ ) yielded white crystals (0.35 g, 15%) of the product.

The analogous methyl compound  $(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  was obtained by a similar procedure to the above except the irradiation was carried out in a closed vessel (see the preparation of  $(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$ ).



### Deprotonation of $(\text{Et}_2\text{SiH}_2)\text{Re}_2(\text{CO})_6$

A sample of  $(\text{Et}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  (0.10 g) was added to 6 ml of 0.5 M ethanolic KOH, and the mixture was stirred at room temperature. The white solid dissolved over 45 minutes to form an orange solution, which gave an orange precipitate upon the addition of  $\text{Ph}_4\text{As}^+\text{Cl}^-$  (0.12 g in 5 ml ethanol). The precipitate was recrystallized from dichloromethane-hexane to yield pure  $[\text{Ph}_4\text{As}^+]_2[(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_6]^-$  (0.10 g).

### Di- $\mu$ -dimethylsilicon-(dihydridotricarbonyl) (tetracarbonyl)-dirhenium, $(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$

A solution of rhenium carbonyl (2.68 g, 7.6 mmol) and dimethylsilane (2.0 g, 33 mmol) in benzene (10 ml) was irradiated with the 450 watt source for 80 hours. At approximately 20 hour intervals the reaction tube was cooled to liquid nitrogen temperature and carbon monoxide was pumped off under vacuum. Removal of excess silane and benzene at reduced pressure left a pale-yellow solid, identified by its infrared spectrum as a mixture of  $\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ ,  $(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  and the product. This mixture was stirred in a chloroform-silicic acid slurry to convert  $\text{Me}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  to  $\text{H}_2\text{Re}_2(\text{CO})_8$ . After filtration and evaporation of the chloroform, the yellow solid was extracted with n-hexane (15 ml); most of the  $\text{H}_2\text{Re}_2(\text{CO})_8$  remained after the extraction. The n-hexane extract was chromato-



graphed on Florisil (50 g, n-hexane elution) to separate the small amount of  $\text{H}_2\text{Re}_2(\text{CO})_8$ . The mixture of  $(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  and product was carefully chromatographed on silicic acid with n-hexane elution. The first fraction off the column was a mixture with  $(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$  predominant (recrystallization of this fraction from n-hexane yielded pure  $(\text{Me}_2\text{SiH}_2)_2\text{Re}_2(\text{CO})_6$ ). The second fraction was pure product. Sublimation of the second fraction ( $50^\circ$ , high vacuum) yielded white crystals (0.15 g, 5%) of pure  $(\text{Me}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$ .

The ethyl analog  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Re}_2(\text{CO})_7$  was obtained by an identical procedure using a closed Carius vessel during irradiation. For this compound a yield of 20% was obtained.

Di- $\mu$ -hydrido-bis(tetracarbonylrhenium),  $\text{H}_2\text{Re}_2(\text{CO})_8$

Silicic acid (5 g) was added to a solution of  $\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8$  (1.0 g) in chloroform (50 ml) and stirred for one hour. Filtration of the mixture and evaporation of solvent at reduced pressure left a yellow solid. Recrystallization from 20 ml n-hexane-dichloromethane ( $-20^\circ$ ) provided yellow crystals (0.60 g, 78%) of  $\text{H}_2\text{Re}_2(\text{CO})_8$ . The exact mass was measured for  $m/e = 600$ : calculated

$$[\text{H}^1_2\text{Re}_2^{374}\text{C}_8^{12}\text{O}_8^{16}] = 599.8869; \text{ found: } 599.8860.$$

$\mu$ -Hydrido- $\mu$ -chloro-bis(tetracarbonylrhenium),  $\text{HClRe}_2(\text{CO})_8$

A solution of  $\text{H}_2\text{Re}_2(\text{CO})_8$  (0.90 g) in carbon tetra-





chloride (50 ml) was heated at 55° for 15 hours. A white solid which precipitated during this interval was identified by its infrared spectrum as  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ .<sup>154</sup> The solution was evaporated at reduced pressure and the residual solid was chromatographed on Florisil (50 g, n-hexane elution) to remove the last traces of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ . Recrystallization from 20 ml n-hexane gave the pure product (0.12 g, 15%).

$\mu$ -Diphenylsilicon-bis(pentacarbonyltungsten),  $\text{Ph}_2\text{SiW}_2(\text{CO})_{10}$

A solution of  $\text{W}(\text{CO})_6$  (2.50 g, 7.1 mmol) and  $\text{Ph}_2\text{SiH}_2$  (1.5 ml, 8.1 mmol) in 150 ml cyclohexane was irradiated (450 watt source) for eleven hours. Removal of solvent left an orange solid which was sublimed (50°, 0.01 mm) to remove unreacted starting materials. The unsublimed orange solid was crystallized twice from 1:1 dichloromethane-n-hexane to afford orange crystals (1.0 g, 34%) of the product. In the mass spectrum the most abundant peak ( $m/e$  830) of the molecular ion was measured: calculated - 829.9068; found - 829.9075.

The methyl analog  $\text{Me}_2\text{SiW}_2(\text{CO})_{10}$  was obtained using a similar procedure to the above except reaction was carried out in a closed Carius vessel with irradiation from the 140 watt source. Irradiation for 45 hours yielded 10% of pure product.





Di-μ-diethylsilicon-bis(hydridotetracarbonyltungsten),  
 $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$

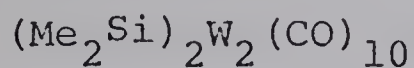
A solution of  $\text{W}(\text{CO})_6$  (2.25 g, 6.4 mmol) and  $\text{Et}_2\text{SiH}_2$  (3.0 ml, 25 mmol) was irradiated (450 watt source) in 150 ml cyclohexane for 2.5 hours. The infrared spectrum of an aliquot of the red solution at this stage showed that it contained  $\text{Et}_2\text{SiW}_2(\text{CO})_{10}$ ,  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$ , and starting materials. Irradiation for an additional 5 hours left  $(\text{Et}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$  as the major product. Cyclohexane was removed at reduced pressure to leave a dark-red oil which was sublimed ( $50^\circ$ , 0.01 mm) to remove  $\text{W}(\text{CO})_6$ . Crystallization of the residue from 25 ml n-hexane at  $-78^\circ$  gave dark crystals of product. Two recrystallizations from n-hexane at  $-20^\circ$  afforded the pure product as yellow crystals (0.35 g, 15%). Exact mass measured for most abundant peak in molecular ion ( $m/e$  766): calculated, 765.9875; found, 765.9855.

Di-μ-diethylsilicon-bis(hydridotetracarbonylmolybdenum),  
 $(\text{Et}_2\text{Si})_2\text{H}_2\text{Mo}_2(\text{CO})_8$

The preparation of this compound was almost identical to the procedure given above for the tungsten analog. Irradiation with the 450 watt source for 5.5 hours yielded yellow crystals of  $(\text{Et}_2\text{Si})_2\text{H}_2\text{Mo}_2(\text{CO})_8$  (20%).



Di-μ-dimethylsilicon-bis(pentacarbonyltungsten),



Dimethylsilane (2.5 g, 42 mmol) was condensed into an evacuated Pyrex tube containing benzene (15 ml) and  $\text{W}(\text{CO})_6$  (1.8 g, 5.1 mmol). The tube was irradiated (140 watt source) for 400 hours with release of pressure every 48 hours while the contents were frozen in liquid nitrogen. Excess dimethylsilane was then distilled off and the orange benzene solution was decanted from undissolved solids; the infrared spectrum of the benzene solution indicated the presence of  $\text{W}(\text{CO})_6$ ,  $(\text{Me}_2\text{Si})_2\text{W}_2(\text{CO})_{10}$ , and  $(\text{Me}_2\text{Si})_2\text{H}_2\text{W}_2(\text{CO})_8$ . Sublimation of the undissolved solids (50°, 0.01 mm) removed  $\text{W}(\text{CO})_6$ ; the unsublimed solid was crystallized from 10 ml n-hexane-dichloromethane (1:1) to form yellow crystals (0.10 g, 5%) of the product.



## CHAPTER IV

### PHOTOCHEMICAL REACTIONS OF MONOFUNCTIONAL SILANES WITH RHENIUM CARBONYL

#### Introduction

In extending the photochemical reactions of silanes with transition metal carbonyls as described in the last Chapter for difunctional silanes ( $R_2SiH_2$ ), this Chapter will describe the photochemical reactions of monofunctional silanes  $Cl_{3-n}R_nSiH$  ( $n = 0, 1, 2, 3$ ) with the dinuclear  $Re_2(CO)_{10}$ . The products obtained were hydrides of the types  $Cl_3SiHRe_2(CO)_9$  and  $HRe_3(CO)_{14}$ . Some of the complexes recounted in the last Chapter were formulated with bent hydrogen-bridges between two rhenium atoms ( $H_2Re_2(CO)_8$  and  $HClRe_2(CO)_8$ ). The possibility of bent bridges between silicon and the transition metal was suggested for the silicon metal hydrides. The complexes to be described in this Chapter can be best formulated with linear Re-H-Re systems; this linear arrangement is well established for the complexes  $HRe_3(CO)_{14}$  and  $HMnRe_2(CO)_{14}$ .<sup>105, 108, 136, 154, 156</sup>

A number of polynuclear transition metal carbonyl hydrides have been formulated with a linear M-H-M system. On the basis of spectroscopic evidence, the compounds  $HRe_3(CO)_{14}$ ,<sup>136, 154</sup>  $HMnRe_2(CO)_{14}$ ,<sup>136, 154</sup> and  $[HM_2(CO)_{10}]^-$  ( $M = Cr, Mo, W$ )<sup>125, 127</sup> were assigned the linear M-H-M





arrangement. The X-ray structures of  $\text{HMnRe}_2(\text{CO})_{14}$ , <sup>17, 105</sup>  $\text{HRe}_3(\text{CO})_{14}$ , <sup>108</sup> and  $[\text{HCr}_2(\text{CO})_{10}]^-$ , <sup>20, 108</sup> have been determined and support the linear formulation; although the hydrogens were not located, the long metal-metal distances of 3.39 Å, 3.30 Å and 3.41 Å respectively are indicative of linear Re-H-Re or Cr-H-Cr lengths. A suggestion has been made that polynuclear transition-metal complexes with direct metal-metal bonds which can be protonated, may have linear metal-hydrogen-metal bonds.<sup>108</sup> Thus known protonated species such as  $[\text{HFe}_2(\text{CO})_8]^-$  <sup>157</sup> and  $\{\text{H}[\text{W}(\text{CO})_3\text{Cp}]_2\}^+$  <sup>158</sup> may contain linear bridges. Heterobinuclear species such as  $[\text{HCrMo}(\text{CO})_{10}]^-$  <sup>125</sup> and  $\text{HReW}(\text{CO})_{10}$  (as yet hypothetical)<sup>159</sup> may also have linear hydrogen bridges.

The bonding in these linear hydrogen-bridged systems has been described as a two-electron three-centre bond.<sup>108</sup> Another description which in effect leads to the same result is that the metal-hydrogen bond of one metal effectively acts as a two-electron donor ligand.<sup>105</sup> Then in the complexes  $\text{HRe}_3(\text{CO})_{14}$  and  $\text{HMnRe}_2(\text{CO})_{14}$ ,  $\text{HRe}(\text{CO})_5$  may be regarded as a neutral ligand (L) which has displaced a radial carbonyl in  $\text{Re}_2(\text{CO})_{10}$  or  $\text{MnRe}(\text{CO})_{10}$  to give  $\text{LRe}_2(\text{CO})_9$  or  $\text{LMnRe}(\text{CO})_9$ . Similarly in  $\text{HM}_2(\text{CO})_{10}^-$ ,  $[\text{HM}(\text{CO})_5]^-$  may be thought of as a two-electron donor ligand to the unsaturated  $\text{M}(\text{CO})_5$  moiety. Treatment of  $\text{HMnRe}_2(\text{CO})_{14}$  and  $\text{HRe}_3(\text{CO})_{14}$  with CO and other ligands has shown that  $\text{HRe}(\text{CO})_5$  is easily





displaced.<sup>154</sup> The dissociation of  $[\text{HM}_2(\text{CO})_{10}]^-$  into  $[\text{HM}(\text{CO})_5]^-$  and  $\text{M}(\text{CO})_5$  has been suggested.<sup>125</sup> The above bonding description complies with the effective atomic number rule.

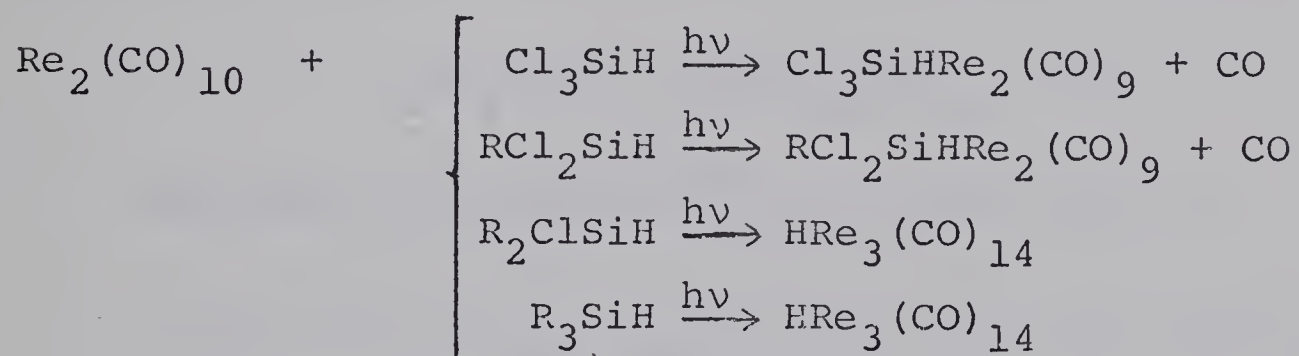
The synthesis and properties of the complexes  $\text{Cl}_{3-n}\text{R}_n\text{SiHRe}_2(\text{CO})_9$  ( $n = 0,1$ ) are now given; the properties of these complexes suggest that a linear Re-H-Re framework is present in these complexes similar to the ones described above.



## R E S U L T S     A N D     D I S C U S S I O N

### 1.     Synthesis

The products obtained from the ultraviolet irradiation of the monofunctional silanes  $\text{Cl}_{3-n}\text{R}_n\text{SiH}$  ( $\text{R} = \text{Ph}, \text{Me}; n = 0, 1, 2, 3$ ) with rhenium carbonyl varied with the number of chlorines ( $3-n$ ). This variation is shown in the following scheme which summarizes the reactions studied.

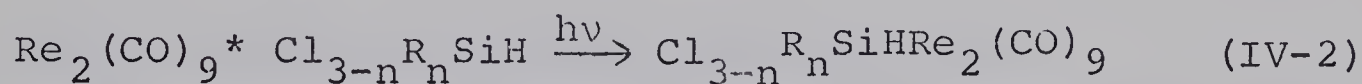
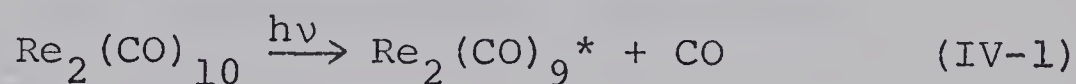


The irradiations were carried out in hexane, benzene or cyclohexane solutions using excess silane (see Experimental for details). The compounds  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{HRe}_3(\text{CO})_{14}$  precipitated out of the reaction solutions. The compounds  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  ( $\text{R} = \text{Ph}, \text{Me}$ ) are more soluble and only small amounts precipitated. The silicon compounds  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  are white crystalline solids; the trichloro derivative is air-stable while the  $\text{RCl}_2\text{Si}$  derivatives are only moderately air-stable. The compound  $\text{HRe}_3(\text{CO})_{14}$  was obtained in good yields (50%) by this one step reaction; this complex was previously synthesized by Kaesz et al.<sup>154</sup> and involved



several tedious steps which resulted in lower yields than reported here.

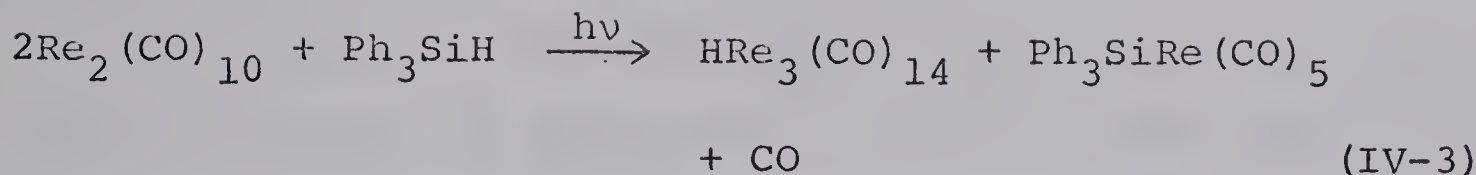
A reasonable mechanism in these photochemical reactions appears to be the initial ejection of a carbon monoxide by a sufficiently energetic photon to form the reactive intermediate  $\text{Re}_2(\text{CO})_9^*$  (IV-1). This intermediate probably then reacts with the silane to form the observed products  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  or  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  (IV-2).



With the silanes  $\text{R}_2\text{ClSiH}$  and  $\text{R}_3\text{SiH}$  the corresponding silicon derivatives  $\text{R}_2\text{ClSiHRe}_2(\text{CO})_9$  and  $\text{R}_3\text{SiHRe}_2(\text{CO})_9$  appeared to be unstable and decomposed to yield  $\text{HRe}_3(\text{CO})_{14}$  as the only isolable product. During the irradiation of  $\text{Me}_2\text{ClSiH}$  with  $\text{Re}_2(\text{CO})_{10}$  infrared evidence for  $\text{Me}_2\text{ClSiHRe}_2(\text{CO})_9$  was obtained but rapid decomposition to  $\text{HRe}_3(\text{CO})_{14}$  occurred on attempted purification. Even during the irradiations of  $\text{RCl}_2\text{SiH}$  with  $\text{Re}_2(\text{CO})_{10}$ , small amounts of  $\text{HRe}_3(\text{CO})_{14}$  were always detected in the reaction mixtures.

When the irradiation of  $\text{Ph}_3\text{SiH}$  with  $\text{Re}_2(\text{CO})_{10}$  was originally carried out the reaction mixture warmed to ca.  $60^\circ$  and appreciable amounts of  $\text{Ph}_3\text{SiRe}(\text{CO})_5$  were obtained. This suggested an overall reaction:

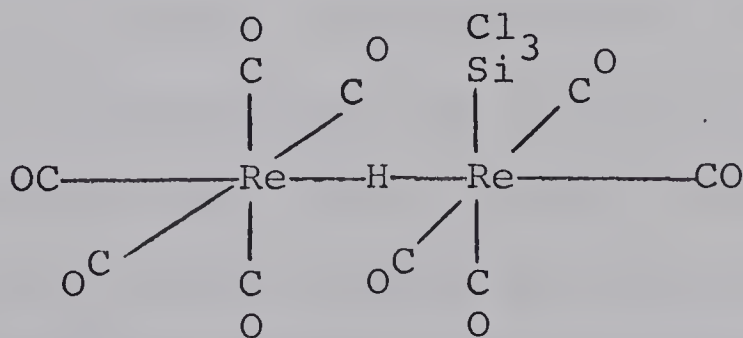




However, it is known that  $\text{Ph}_3\text{SiRe}(\text{CO})_5$  is formed by the thermal reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{Ph}_3\text{SiH}$ .<sup>10</sup> When the photolysis was carried out maintaining the reaction solution below  $20^\circ$ , no  $\text{Ph}_3\text{SiRe}(\text{CO})_5$  was detected;  $\text{HRe}_3(\text{CO})_{14}$  was the only carbonyl compound obtained. The fate of the  $\text{Ph}_3\text{Si}$  moiety in this reaction remains unresolved.

## 2. Spectroscopic Properties and Structure.

The spectroscopic properties of  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{HRe}_2(\text{CO})_9$  ( $\text{R} = \text{Ph}, \text{Me}$ ) suggest that the most probable formulation for these complexes is the idealized  $\text{C}_s$  structure as shown below for  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  with the linear  $\text{Re-H-Re}$  arrangement. Although the eclipsed conformation of the carbonyl groups is shown, the staggered form is just as likely; the spectroscopic properties are consistent with either conformation.







The proposed structure 38 can be derived from the known structures of  $\text{HMnRe}_2(\text{CO})_{14}$ , <sup>17</sup> <sup>105</sup> or  $\text{HRe}_3(\text{CO})_{14}$  <sup>108</sup> by replacing the  $\text{Mn}(\text{CO})_5$  or  $\text{Re}(\text{CO})_5$  group with a  $\text{Cl}_3\text{Si}$  fragment. In the  $\text{HRe}_2(\text{CO})_9$  part of the molecule the carbonyls are in the eclipsed configuration in  $\text{HMnRe}_2(\text{CO})_{14}$  and staggered in  $\text{HRe}_3(\text{CO})_{14}$ . The spectral properties of  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  will now be discussed and compared to those of  $\text{HRe}_3(\text{CO})_{14}$  and other carbonyl hydrides with well established structures.

### Nmr Spectra

The chemical shifts of the hydride protons are given in Table XI; these high  $\tau$  values make a terminally bonded hydrogen appear unlikely, as discussed in Chapter III. The hydrides  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  have higher chemical shifts than any of the silicon compounds discussed in the preceding Chapter; this is at least suggestive of a linear  $\text{Re-H-Re}$  bridge. However, a clear cut distinction cannot be made between a bent and a linear hydrogen bridge between two transition metals using chemical shifts alone. This is borne out by the fact that  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  (bent bridges) and  $\text{HRe}_3(\text{CO})_{14}$  (linear bridge) absorb at almost the same field of ca.  $\tau$  27 <sup>160</sup> and  $\tau$  26.25 <sup>154</sup> respectively. The other spectroscopic aspects, which are discussed below, indicate that the linear bridged system is the favored one for



TABLE XINMR DATA FOR  $\text{XRe}_2(\text{CO})_9$  DERIVATIVES

Compound	$\tau$ value of high-field proton
$\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$	22.45 ( $\text{CDCl}_3$ )
$\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9^{\text{a}}$	24.44 ( $\text{CDCl}_3$ )
$\text{PhCl}_2\text{SiHRe}_2(\text{CO})_9^{\text{b}}$	24.60 ( $\text{CDCl}_3$ )
$\text{HRe}_3(\text{CO})_{14}$	26.25 <sup>154</sup>

<sup>a</sup> Methyl resonance a sharp singlet at  $\tau$  8.78.

<sup>b</sup> Phenyl region is a complex multiplet.



for  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$ .

If the  $\text{HRe}_2(\text{CO})_9$  parts of the molecule in the four compounds in Table XI are bonded in a similar manner (linear  $\text{Re-H-Re}$ ), then the chemical shifts of the hydride ligand may depend mainly on the electronegativity of the group attached ( $\text{Cl}_3\text{Si}$ ,  $\text{RCl}_2\text{Si}$ ,  $\text{Re}(\text{CO})_5$ ). The observed chemical shifts are consistent with this supposition and shows a shift to lower field with increased electronegativity of the group attached.

The nmr spectrum of  $\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$  shows a sharp singlet for the methyl protons; this appears to rule out formulations such as  $\text{Si-H-Re}$  or  $\text{Si} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{Re}$  where the hydride ligand is proximate to the silicon moiety.

### Infrared Spectra

The infrared spectra in the carbonyl stretching region of the complexes  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$ ,  $\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$  and  $\text{PhCl}_2\text{SiHRe}_2(\text{CO})_9$  are shown in Figures 36-38; the frequencies are given in Table XII. The band patterns for the three compounds are very similar and parallel structures are indicated. The number of carbonyl bands observed is 7 or 8; a maximum nine bands is predicted for the  $\text{C}_s$  structure <sup>38</sup> (either eclipsed or staggered predicts the same number of bands). If the silicon moiety was in an axial position as in <sup>39</sup> (idealized  $\text{C}_{4v}$  symmetry), only five carbonyl stretching bands are expected. The  $\text{C}_{4v}$  structure can therefore



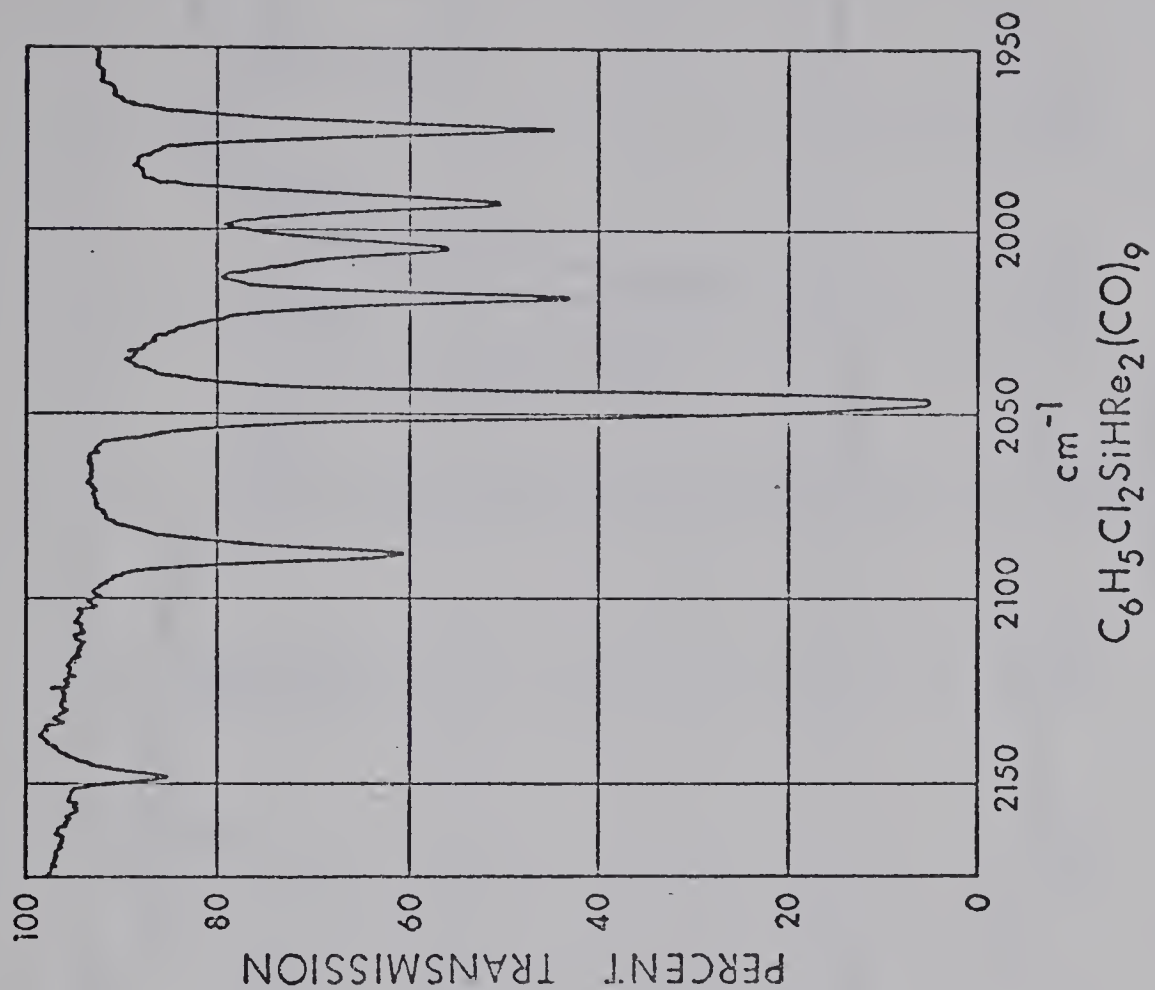


FIGURE 37

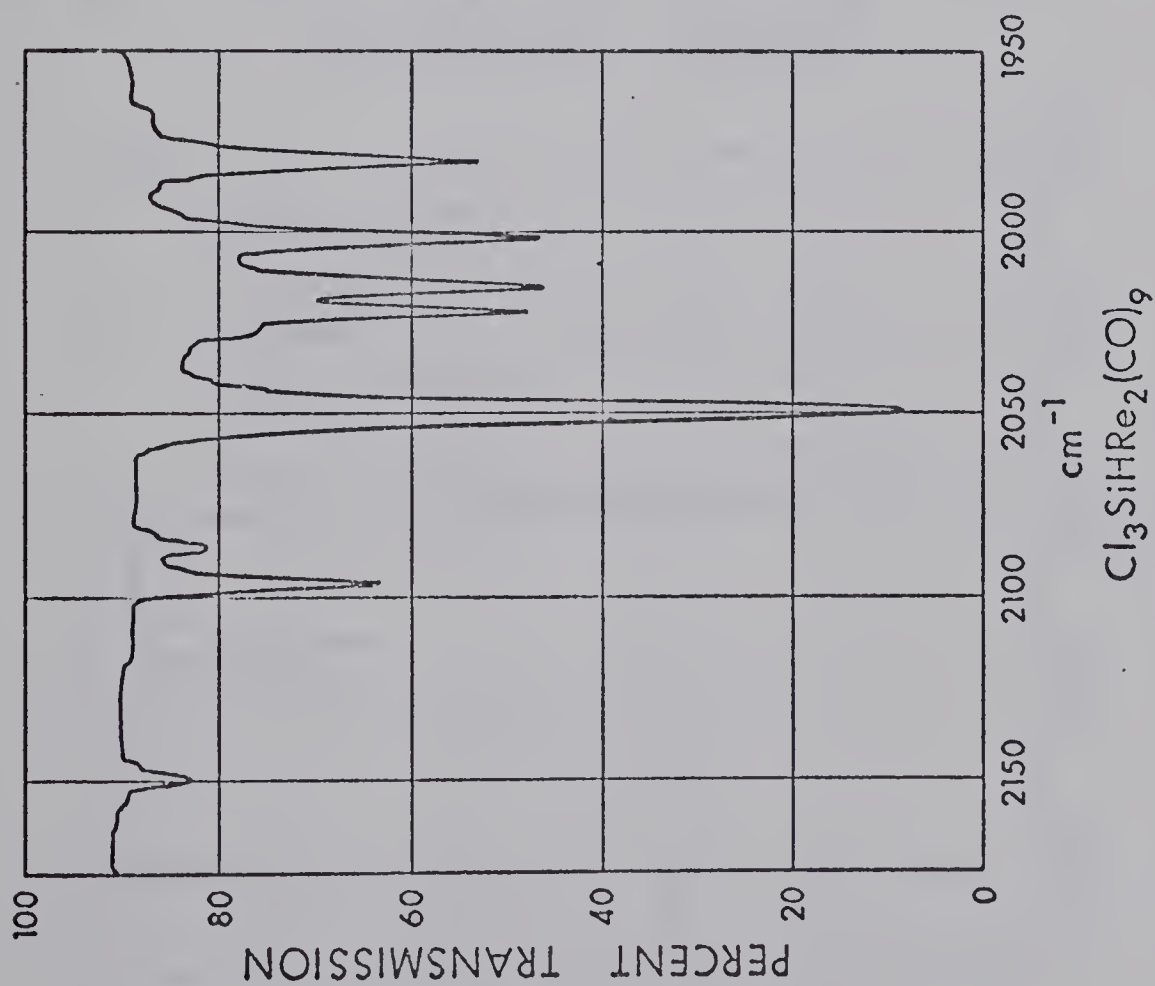


FIGURE 36





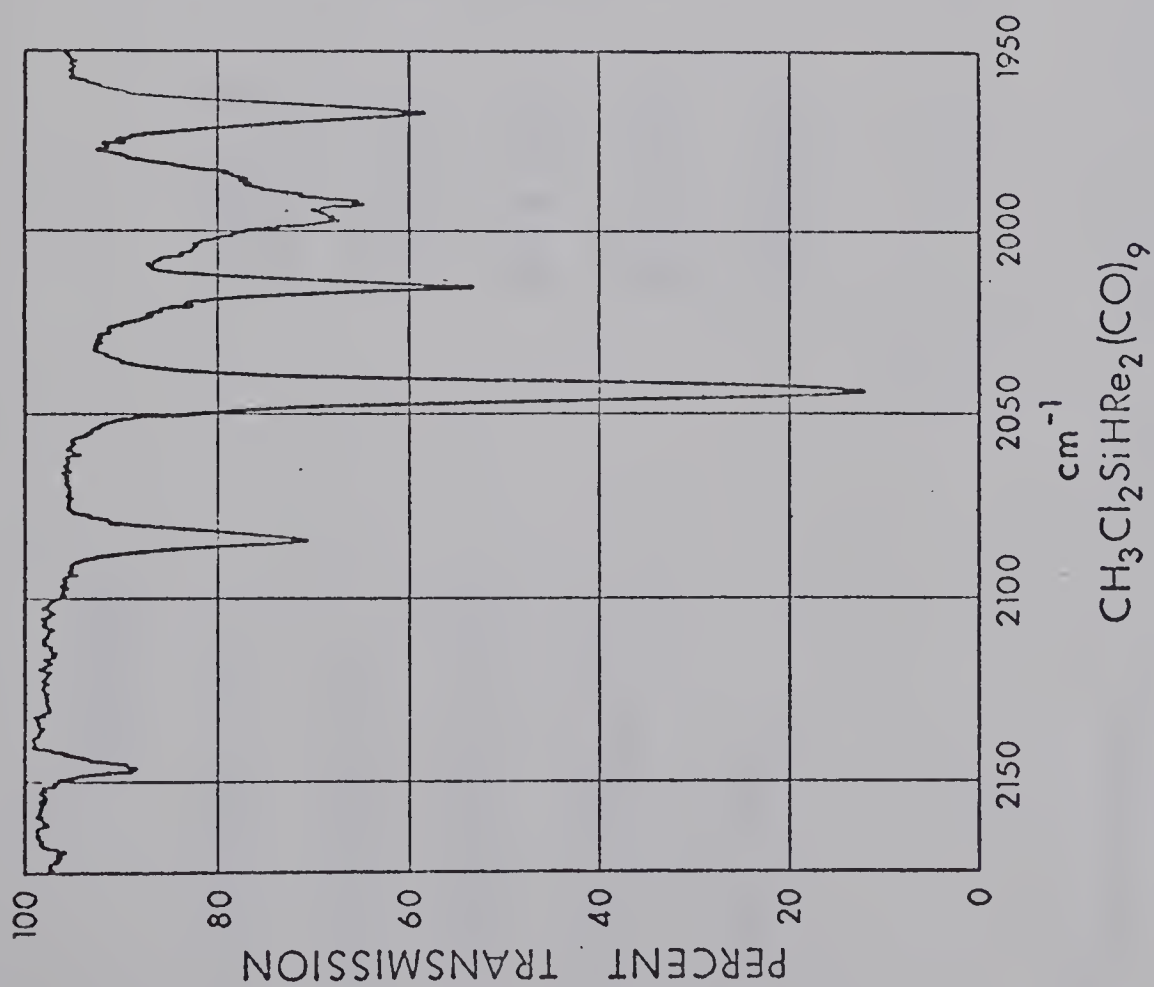


FIGURE 38

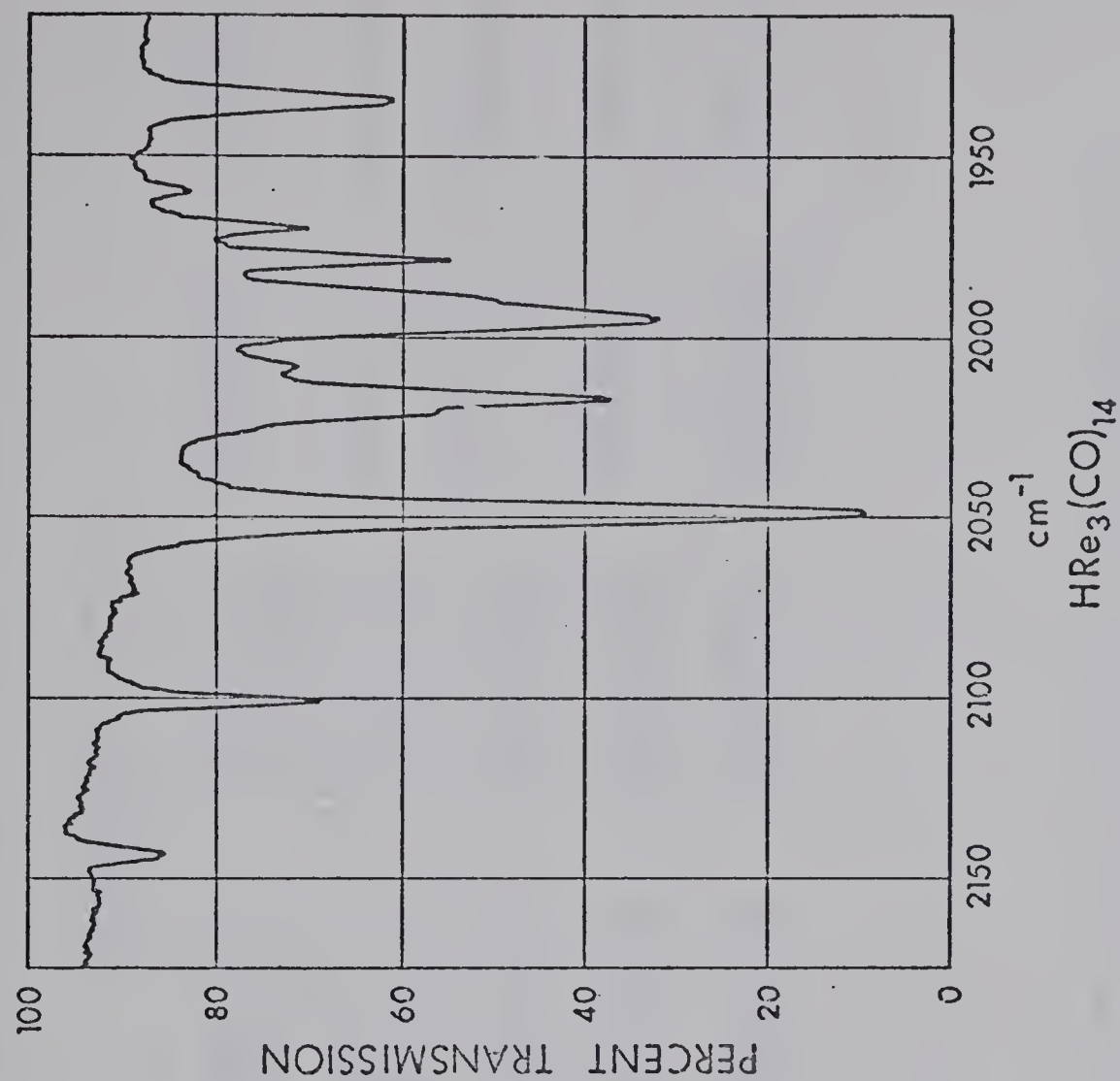


FIGURE 39



TABLE XII

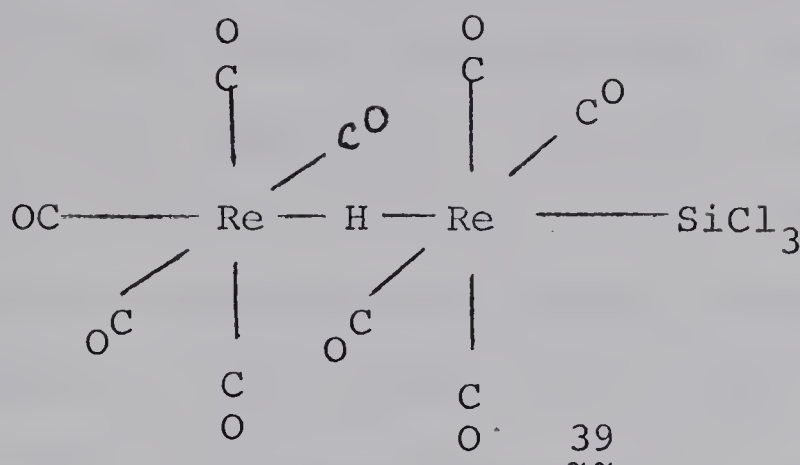
INFRARED CARBONYL STRETCHING FREQUENCIES OF POLYNUCLEAR RHENIUM CARBONYL HYDRIDES

Compound	Frequency (cm <sup>-1</sup> ) <sup>a</sup>			
Cl <sub>3</sub> SiHRe <sub>2</sub> (CO) <sub>9</sub>	2150(1.4)	2095(3.6)	2085(1.6)	2047(10.0)
	2012(5.6)	1999(5.6)	1978(4.8)	2019(5.4)
Cl <sub>3</sub> SiDRe <sub>2</sub> (CO) <sub>9</sub>	2151(0.8)	2095(2.4)	2086(0.8)	2048(10.0)
	2012(4.9)	2000(4.4)	1979(3.6)	2020(3.5)
PhCl <sub>2</sub> SiHRe <sub>2</sub> (CO) <sub>9</sub>	2149(1.0)	2087(3.9)	2046(10.)	2017(5.8)
	2004(4.3)	1991(5.0)	1971(5.6)	2004(4.3)
MeCl <sub>2</sub> SiHRe <sub>2</sub> (CO) <sub>9</sub>	2148(1.0)	2086(3.2)	2044(10.0)	2016(5.0)
	1992(3.6)	1985(2.3)	1968(4.6)	1998(3.5)
HRe <sub>3</sub> (CO) <sub>14</sub>	2145(1.2)	2101(2.5)	2048(10.0)	1992(7.0)
	1975(4.2)	1966(2.3)	1956(1.5)	1933(4.0)

<sup>a</sup> Cyclohexane solutions. Figures in parenthesis are relative band heights on a transmittance scale.



be discounted.



The deuterated complex  $\text{Cl}_3\text{SiDRe}_2(\text{CO})_9$  (prepared from  $\text{Cl}_3\text{SiD}$ ) shows a carbonyl stretching band pattern which is almost identical to that of the hydride except for small shifts ( $\leq 2 \text{ cm}^{-1}$ ) in some of the band positions (see Table XII). There were no other observable differences in the infrared spectra (H vs D) in the region  $800 - 2200 \text{ cm}^{-1}$ . As in the hydrides discussed in Chapter III, the hydride mode appears to be infrared "inactive". Kaesz et al.<sup>154</sup> have been unable to observe any hydrogen mode for  $\text{HRe}_3(\text{CO})_{14}$  in the infrared spectrum. A careful infrared and Raman study of  $[\text{HCr}_2(\text{CO})_{10}]^-$  and  $[\text{DCr}_2(\text{CO})_{10}]^-$  by Edgell and Paaue<sup>161</sup> failed to locate the hydride or deuteride modes.

Detailed examination of the carbonyl stretching band patterns and frequencies of the complexes  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$ ,  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  and  $\text{HRe}_3(\text{CO})_{14}$  (Figures 36-39, Table XII) shows some features characteristic of all four complexes which may possibly be interpreted as due to structural similarities. For each complex in Table XII, the relative intensities and band frequencies of the highest energy band



(A), the most intense band (B), and the band next to the most intense band on the low frequency side (C) are very similar among all the complexes. These are tabulated in Table XIII. The intensity pattern of these three bands strongly resembles the pattern of  $\text{XM}(\text{CO})_5$  complexes as discussed in Chapter II (see Figures 1-3). Then for the complexes in Table XIII the three bands may be assigned to the  $\text{HRe}(\text{CO})_5$  moiety, the common feature of the complexes (presuming the linear  $\text{Re-H-Re}$  arrangement).

If  $\text{HRe}(\text{CO})_5$  acts as a neutral two-electron donor ligand as suggested by Kaesz et al.<sup>105</sup> for  $\text{HRe}_3(\text{CO})_{14}$ , there will be a flow of electrons away from the  $\text{HRe}(\text{CO})_5$  moiety.



In the above case as well as for the silicon compounds, the carbonyl bands due to the  $\text{HRe}(\text{CO})_5$  moieties should be of higher energy than the corresponding bands in  $\text{HRe}(\text{CO})_5$  itself; Table XIII is in agreement with this expectation.

In  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  the four bands at 2095, 2012, 1999 and 1978  $\text{cm}^{-1}$  are presumably due to the cis- $[(\text{CO})_4\text{Re}^{\delta+} \text{---} \text{SiCl}_3^{\delta-}]$  moiety; for  $\text{PhCl}_2\text{SiHRe}_2(\text{CO})_9$  these four bands are shifted to 2087, 2004, 1991 and 1971  $\text{cm}^{-1}$  respectively. These shifts are much greater than the shifts of the bands which were assigned to the  $\text{HRe}(\text{CO})_5$  groups (see Table XIII). This observation is in agreement with the proposed structure;





TABLE XIII

CARBONYL STRETCHING FREQUENCIES ASSIGNED TO THE  $\text{HRe}(\text{CO})_5$ 

<u>Compound</u>	<u>MOIETY</u>		
	Carbonyl Stretching Frequencies ( $\text{cm}^{-1}$ ) <sup>a</sup>		
	(A)	(B)	(C)
$\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$	2150 (1.4)	2047 (10.0)	2019 (5.4)
$\text{PhCl}_2\text{SiHRe}_2(\text{CO})_9$	2149 (1.0)	2046 (10.0)	2017 (5.8)
$\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$	2148 (1.0)	2044 (10.0)	2016 (5.0)
$\text{HRe}_3(\text{CO})_{14}$	2145 (1.2)	2048 (10.0)	2014 (5.6)
$\text{HRe}(\text{CO})_5^{162}$	2131 (vw)	2014 (s)	2005 (m)

<sup>a</sup>  
Cyclohexane solutions



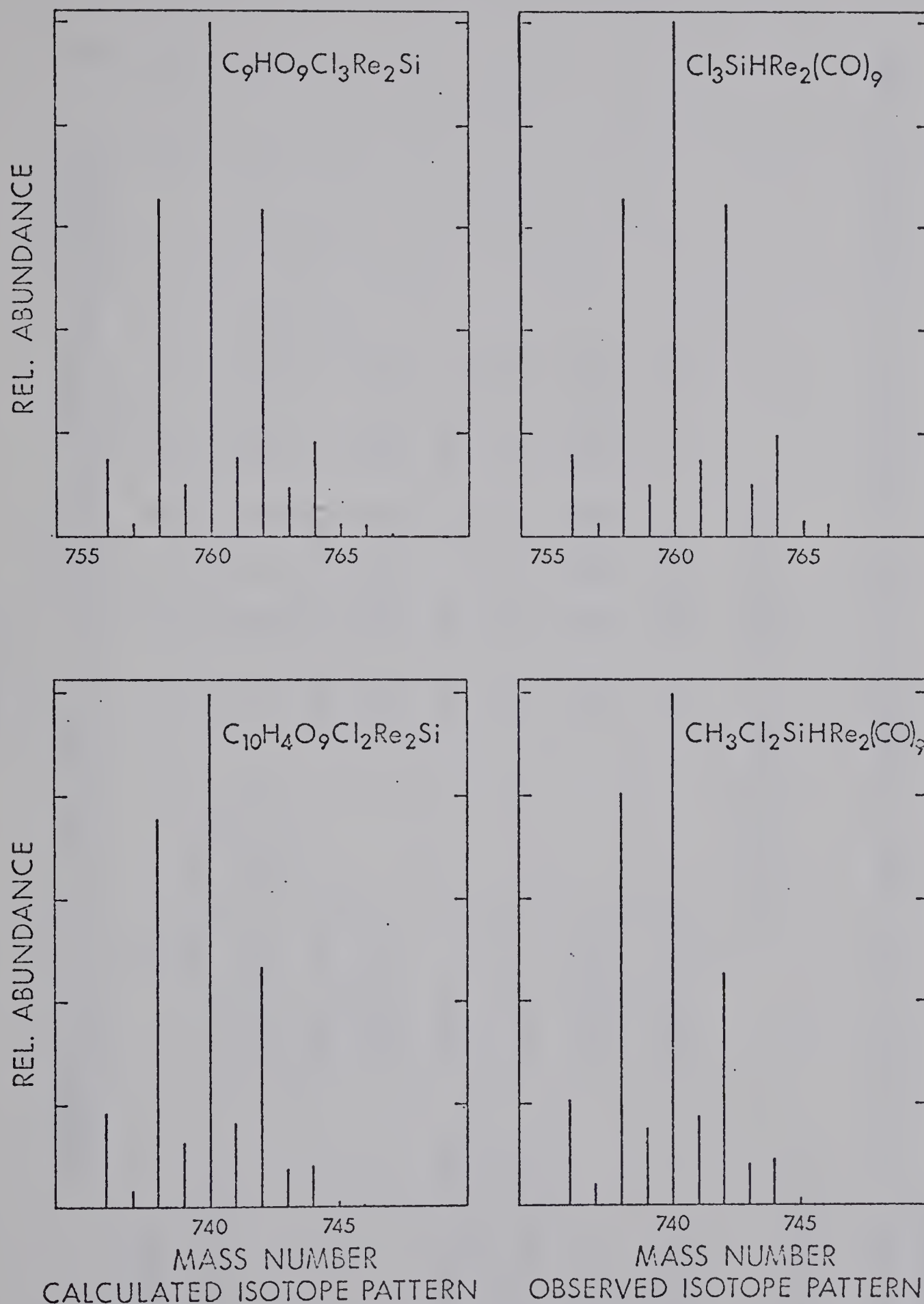
the frequencies due to the  $\text{Re}(\text{CO})_4$  group should be more sensitive to the silyl ligand than the far removed carbonyl groups on the  $\text{HRe}(\text{CO})_5$  moiety.

### Mass Spectra

Mass spectrometry was again used as the major means of determining the exact molecular formulae of the complexes as was described in Chapter III. The calculated and observed molecular ion isotope patterns of  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$  are shown in Figure 40.

The mass spectral fragmentation patterns give convincing support to the linear Re-H-Re formulation in the silicon compounds. Table XIV summarizes the hydrogen loss percentages of the various fragmentation series in the spectrum of  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$ . The complexes  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  exhibited mass spectral fragmentation series very similar to  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$ . The long series beginning with the parent ion  $[\text{Cl}_3\text{SiHRe}_2(\text{CO})_9]^+$  and the stepwise loss of nine carbonyl groups shows hydrogen loss only after seven carbonyls have been lost (Table XIV). The only other polynuclear metal carbonyl hydrides which have been reported to show similar fragmentations are the complexes  $\text{HRe}_3(\text{CO})_{14}$ ,  $^{136}\text{HMnRe}_2(\text{CO})_{14}$ ,  $^{136}\text{HFeCo}_3(\text{CO})_{12}$ ,  $^{163}$  and  $^{163}\text{HRuCo}_3(\text{CO})_{12}$ . The first two complexes almost certainly have a linear Re-H-Re system





Calculated and Observed Mass Spectral Isotope Patterns

FIGURE 40



TABLE XIV

HYDROGEN LOSS IN MASS SPECTRA OF RHENIUM CARBONYL HYDRIDES

Compound	Ion	<u>n</u>									
		0	1	2	3	4	5	6	7	8	9
$\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$	$[\text{Cl}_3\text{SiHRe}_2(\text{CO})_n]^+$	25	10	5	0	0	0	0	0	a	0
	$[\text{Cl}_2\text{SiHRe}_2(\text{CO})_n]^+$	70	60	b	b	35	b	15	0	b	0
	$[\text{HRe}_2(\text{CO})_n]^+$	95	75	b	60	70	70	80	75	65	b
	$[\text{HRe}(\text{CO})_n]^+$	95	85	60	75	65	60				
$\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$	$[\text{HRe}(\text{CO})_n]^+$	90	75	b	65	70	55				
$\text{PhCl}_2\text{SiHRe}_2(\text{CO})_9$	$[\text{HRe}(\text{CO})_n]^+$	90	75	45	65	60	40				
$\text{HRe}(\text{CO})_5^c$	$[\text{HRe}(\text{CO})_n]^+$	95	70	35	50	25	15				
$\text{HRe}_3(\text{CO})_{14}$	$[\text{HRe}(\text{CO})_n]^+$	90	80	35	50	45	20				

<sup>a</sup> Not observed

<sup>b</sup> Very weak and overlap with other fragments made calculation of hydrogen loss impossible.

<sup>c</sup> Calculated from data in reference 142.





as previously discussed; the structure of the latter two complexes is less certain but a structure with the hydrogen located in the centre of a tetrahedral cage of metal atoms has been proposed.<sup>163</sup> Compounds with bent hydrogen bridges between two transition metals such as  $\text{H}_2\text{Re}_2(\text{CO})_8$ ,  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ , and  $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$  showed the molecular ion with no hydrogen loss but hydrogen loss was observed after the loss of one to three carbonyl groups as discussed in the previous Chapter. It appears that hydrogen loss is much more competitive with CO loss in the bent bridges than in the linear bridges and this seems to be a criterion for distinguishing the two types.

Other fragmentation series observed in the mass spectrum of  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  are the ones beginning with  $[\text{Cl}_2\text{SiHRe}_2(\text{CO})_9]^+$ ,  $[\text{HRe}_2(\text{CO})_9]^+$  and  $[\text{HRe}(\text{CO})_5]^+$ . The latter two series display competitive hydrogen loss in all fragments (see Table XIV); this is similar to the fragmentation observed in  $\text{HRe}_3(\text{CO})_{14}$ .<sup>136</sup> The fact that  $[\text{HRe}(\text{CO})_5]^+$  is observed at all strongly suggests that the  $\text{HRe}(\text{CO})_5$  moiety is present in the molecule, although one cannot completely discount the possibility of CO transfer during fragmentation;<sup>136,163,164</sup> however, the relative intensities within the  $[\text{HRe}(\text{CO})_n]^+$  series suggest that  $[\text{HRe}(\text{CO})_5]^+$  is not due to CO transfer. Table XIV compares the  $[\text{HRe}(\text{CO})_n]^+$  series among the various



complexes (including  $\text{HRe}(\text{CO})_5$ ). The silicon compounds show a less intense spectrum for this series than does  $\text{HRe}_3(\text{CO})_{14}$  where the  $[\text{HRe}(\text{CO})_n]^+$  series is the most intense in the spectrum.<sup>136</sup> This is reflected in the fact that donor ligands react with  $\text{HRe}_3(\text{CO})_{14}$  under mild conditions to displace  $\text{HRe}(\text{CO})_5$ <sup>165</sup> while the silicon compounds are much less reactive (see below). However, Table XIV shows that the hydrogen loss percentages for the  $[\text{HRe}(\text{CO})_n]^+$  series are all similar.

### Chemical Properties

The complexes  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  were much less reactive than  $\text{HRe}_3(\text{CO})_{14}$ . A stirred hexane solution of  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  under 1000 psi CO pressure showed no observable reaction after four days. The complex  $\text{HRe}_3(\text{CO})_{14}$  has been shown to react with CO at atmospheric pressure to give  $\text{HRe}(\text{CO})_5$  and  $\text{Re}_2(\text{CO})_{10}$  after 2 days.<sup>165</sup> With triphenylphosphine,  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  reacted only slowly at  $120^\circ$ ; there was much decomposition and the only compound identified (by infrared and mass spectroscopy) was  $(\text{Ph}_3\text{P})_2(\text{CO})_3\text{ReH}$ .<sup>166</sup> Because of the high temperature needed for reaction any  $\text{HRe}(\text{CO})_5$  formed would probably react with the phosphine to form the observed product.<sup>167</sup>

In summing up, the properties of the complexes  $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$  and  $\text{RCl}_2\text{SiHRe}_2(\text{CO})_9$  suggest that the most



probable structure has  $C_s$  symmetry with a linear Re-H-Re bridge as was shown in 38. An X-ray structure determination of one of these compounds is desirable for the establishment of the correct structure. However, numerous attempts to grow crystals of  $Cl_3SiHRe_2(CO)_9$  failed to give samples suitable for X-ray analysis; although physically attractive, the crystals were found to be twinned on close examination.<sup>168</sup>



## EXPERIMENTAL

### General Procedure and Apparatus

A nitrogen atmosphere was maintained during all reactions and during work-up procedures by the use of Schlenk apparatus. Ultraviolet irradiations were carried out as previously described in Chapter III.

Melting points, microanalyses, infrared, nmr and mass spectra were obtained as previously described. The results are summarized in Table XV (melting points and microanalytical data), Table XII (infrared carbonyl stretching frequencies), Table XI (nmr), and Table XIV (mass spectral data).

### Materials

Rhenium carbonyl was purchased from Pressure Chemical Company, Pittsburg, Pa. Silanes were obtained from Pierce Chemical Company, Rockford, Illinois. The deuterated trichlorosilane ( $\text{DSiCl}_3$ ) was synthesized by Merck, Sharp and Dohme of Canada Ltd., Montreal. Hydrocarbon solvents were of reagent grade and were dried over sodium wire and saturated with dry nitrogen prior to use.

### Procedures

#### Hydrido(trichlorosilyl)nonacarbonyldirhenium, $\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$

A magnetically stirred solution of rhenium carbonyl (2.25 g, 3.5 mmol) and trichlorosilane (1.0 ml, 10 mmol) in 50 ml n-hexane was irradiated with the 140 watt source for







TABLE XV

## MELTING POINTS, YIELDS, COLORS, AND ANALYTICAL RESULTS

Compound	Mp	Yield (%)	Color	Calculated %			Found %		
				C	H	Cl	C	H	Cl
$\text{Cl}_3\text{SiHRe}_2(\text{CO})_9$	155 dec	55	white	14.25	0.13	14.00	14.20	0.16	14.40
$\text{Cl}_3\text{SiDRe}_2(\text{CO})_9$	154-155 dec	50	white	14.20	0.27	13.97	14.63	0.36	14.47
$\text{PhCl}_2\text{SiHRe}_2(\text{CO})_9$	130-132	50	white	22.49	0.75	8.84	22.67	0.96	8.42
$\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$	108-110	35	white	16.25	0.55	9.59	16.48	0.73	9.70
$\text{HRe}_3(\text{CO})_{14}^a$	-	50	yellow	17.66	0.11	-	17.50	0.25	-

<sup>a</sup>

Infrared and mass spectra were the same as reported in references 154 and 136.



six hours maintaining the reaction solution at ca. 15°. Some of the product precipitated as a white powder. Solvent and excess trichlorosilane were evaporated at reduced pressure and the residual solid was sublimed (50°, 0.01 mm) to remove unreacted rhenium carbonyl. Two recrystallizations from n-hexane-dichloromethane afforded white crystals of the product (1.40 g).

The deuterated analog  $\text{Cl}_3\text{SiDRe}_2(\text{CO})_9$  was prepared by an identical procedure using  $\text{Cl}_3\text{SiD}$ ; using similar quantities to the above a 50% yield of the product was obtained.

Hydrido(methyldichlorosilyl)nonacarbonyldirhenium,



A Carius tube (fitted with the Teflon valve as described in Chapter III) containing rhenium carbonyl (1.44 g, 2.20 mmol) and methyldichlorosilane (2.0 g, 18 mmol) was irradiated with the 450 watt source for 12 hours. Carbon monoxide pressure was released every two hours. Unreacted methyldichlorosilane was distilled off on a vacuum system and the residual solid was sublimed at 55° to remove unreacted rhenium carbonyl. Three recrystallizations from n-hexane afforded white crystals (0.60 g) of pure  $\text{MeCl}_2\text{SiHRe}_2(\text{CO})_9$ .

Hydrido(phenyldichlorosilyl)nonacarbonyldirhenium,



A solution of rhenium carbonyl (1.10 g, 1.70 mmol)



and phenyldichlorosilane (1.0 g, 5.6 mmol) in 50 ml cyclohexane was irradiated for 4.5 hours with the 140 watt source. The solution was maintained at ca. 15° during the irradiation. Solvent and starting materials were then removed by evaporation at reduced pressure and sublimation at 50°. Unsublimed solid was recrystallized twice from n-hexane to yield 0.40 g of the product.

Hydridotetradecacarbonyltrirhenium,  $\text{HRe}_3(\text{CO})_{14}$ .

Eighteen hours' irradiation (140 watt source) of a solution of rhenium carbonyl (1.58 g, 2.4 mmol) and triphenylsilane (0.70 g, 2.7 mmol) in 50 ml benzene gave a yellow solution. Benzene was evaporated at reduced pressure and the residue was sublimed at 60° (0.01 mm) to remove unreacted starting materials. The unsublimed yellow solid was recrystallized from dichloromethane-n-hexane to afford yellow crystals of the product (0.70 g).



## CHAPTER V

### PHOTOCHEMICAL REACTIONS OF THE $\pi$ (CYCLOPENTADIENYL) TRICARBONYLS OF MANGANESE AND RHENIUM: PREPARATION AND PROPERTIES OF $\text{Cp}_2\text{Re}_2(\text{CO})_5$ AND SILICON DERIVATIVES.

This Chapter will describe some photochemical reactions of  $\text{CpRe}(\text{CO})_3$  and  $\text{CpMn}(\text{CO})_3$ . The first portion reports the synthesis and properties of the single carbonyl-bridged species  $\text{Cp}_2\text{Re}_2(\text{CO})_5$ . The second and larger part details the preparation and properties of silicon metal hydrides of the type  $\text{R}_3\text{SiHM}(\text{CO})_2\text{Cp}$  ( $\text{M} = \text{Mn}, \text{Re}$ ). The deprotonation of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  is also described; this deprotonation has led to the isolation of both cis and trans forms of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ .

#### A. The Complex $\text{Cp}_2\text{Re}_2(\text{CO})_5$

##### Introduction

The last two Chapters have shown that carbon monoxide in transition metal carbonyls can be photochemically displaced by silanes. In the absence of other ligands such as silanes, photochemically or thermally initiated reactions can lead to polynuclear derivatives with the loss of one or more carbonyls. Some examples of thermal reaction products are the tetrameric  $[\text{CpFeCO}]_4$  from  $[\text{CpFe}(\text{CO})_2]_2$ ,<sup>169</sup> and  $\text{Cp}_3\text{Ni}_3(\text{CO})_2$  from  $[\text{CpNiCO}]_2$ .<sup>170</sup> The irradiation of  $\text{Fe}(\text{CO})_5$  to yield  $\text{Fe}_2(\text{CO})_9$  was first reported in 1891<sup>171</sup> and the







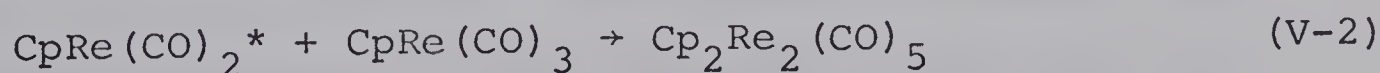
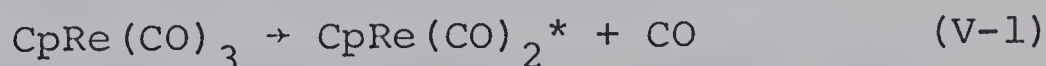
stoichiometry was established in 1905,<sup>172</sup> but the preparation of the authentic second and third row congeners  $\text{Ru}_2(\text{CO})_9$  and  $\text{Os}_2(\text{CO})_9$  has only been reported recently from this laboratory by Moss and Graham.<sup>173,174</sup> The ultraviolet irradiations of  $\text{CpM}(\text{CO})_2$  ( $\text{M} = \text{Co}, \text{Rh}$ ) have given various products: irradiation of  $\text{CpCo}(\text{CO})_2$  has yielded  $[\text{CpCoCO}]_3$ ;<sup>169</sup> irradiation of  $\text{CpRh}(\text{CO})_2$  has given  $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ <sup>175</sup> and a mixture of two geometrical isomers with stoichiometry  $[\text{CpRhCO}]_3$ .<sup>176, 177</sup>

The irradiation of  $\text{CpRe}(\text{CO})_3$  to afford  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  will now be described; the properties of  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  indicate that the most probable structure is one with a single rhenium-rhenium bond supported by a single carbonyl bridge.

### Results and Discussion

Ultraviolet irradiation of a cyclohexane solution of  $\text{CpRe}(\text{CO})_3$  afforded yellow, air-stable crystals of  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  in 10% yield. During the irradiation most of the sparingly soluble product precipitated from solution as a yellow powder.

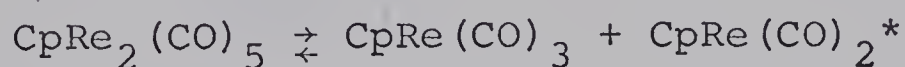
Similar to the previous Chapters a reasonable mechanism for the formation of the product is shown below in (V-1) and (V-2).





In equation V-2  $\text{CpRe}(\text{CO})_3$  acts as a nucleophile which reacts with the electronically unsaturated  $\text{CpRe}(\text{CO})_2^*$ ; the observed product can then be obtained by a shift of one of the carbonyls on the  $\text{CpRe}(\text{CO})_3$  moiety into a bridging position. If silanes are present, the reactive intermediate  $\text{CpRe}(\text{CO})_2^*$  can react to form silicon complexes; these reactions are discussed in the next section.

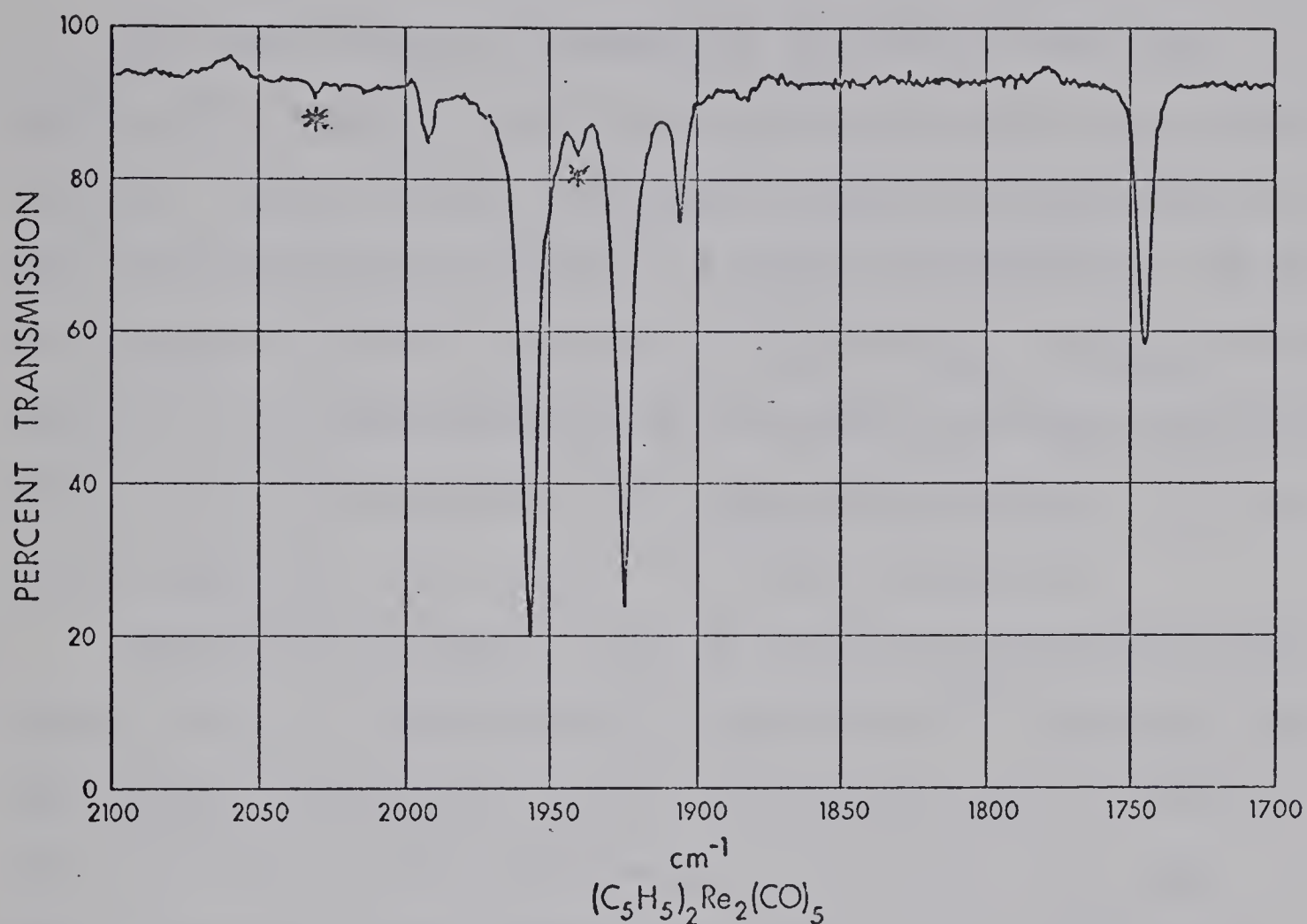
Although the complex  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  is very stable in the solid state, it decomposes slowly in solution. Even immediately after dissolving, weak peaks due to  $\text{CpRe}(\text{CO})_3$  appear and grow on standing (see Figure 41,  $\text{CpRe}(\text{CO})_3$  peaks are labelled with asterisks). It appears that in solution  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  dissociates to  $\text{CpRe}(\text{CO})_3$  and  $\text{CpRe}(\text{CO})_2^*$ ; the unsaturated species appears unstable and decomposes (no carbonyl bands were observed which could be assigned to  $\text{CpRe}(\text{CO})_2^*$ ).



With triphenylphosphine  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  reacts cleanly to yield equimolar amounts of  $\text{CpRe}(\text{CO})_3$  and  $\text{CpRe}(\text{CO})_2\text{PPh}_3$ ; this provides support for the above dissociation.

The infrared spectrum of  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  in the carbonyl stretching region (Figure 41) shows five bands, four terminal and one bridging. This spectrum suggests that the structure consists of one bridging carbonyl and four





Bands labelled with asterisks are due to  $\text{CpRe}(\text{CO})_3$  (see text)

FIGURE 41

terminal carbonyl groups. In the 100 MHz nmr spectrum a single sharp peak (width at  $\frac{1}{2}$  height = 0.3 Hz) was observed at  $\tau$  4.65 for the cyclopentadienyl protons. This indicates that the complex most probably exists predominantly in one conformation in solution. The mass spectrum showed the molecular ion and the fragmentation series corresponding to the loss of five carbonyls. The other main fragmentation series was the one beginning with  $[\text{CpRe}(\text{CO})_3]^+$ , which is

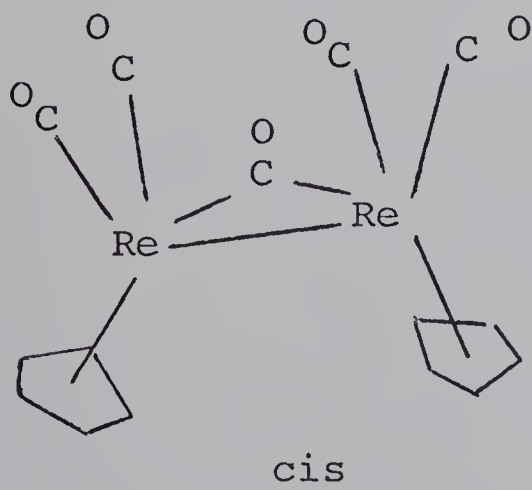




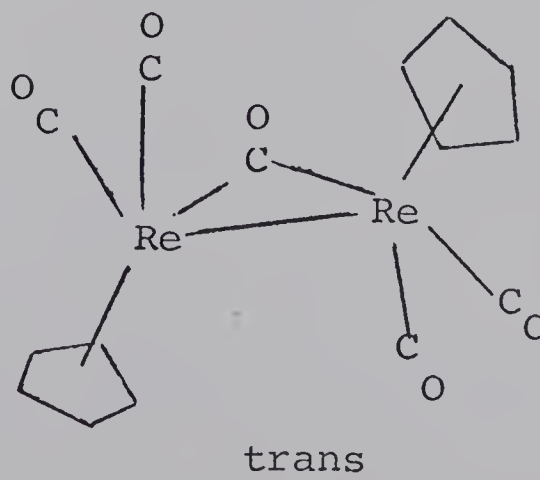
consistent with the presence of the bridging carbonyl.<sup>142</sup>

The spectroscopic properties discussed above for  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  suggest that the structure consists of a single carbonyl bridge across the rhenium-rhenium single bond with the cyclopentadienyl rings in a trans arrangement. The cis and trans structures are shown in 40 and 41; the cis arrangement has  $\text{C}_{2v}$  symmetry and three terminal carbonyl stretching bands are predicted while the trans configuration ( $\text{C}_s$  symmetry) predicts four bands, the number observed.

Preliminary results from an X-ray structure determination by Dr. A. Foust in this department<sup>178</sup> indicate that the trans configuration of the cyclopentadienyl rings is the one found in the solid state as shown in 41. The rhenium-rhenium bond length was found to be  $2.95 \text{ \AA}$  which is consistent with a single bond although somewhat shorter than  $3.02 \text{ \AA}$  length in  $\text{Re}_2(\text{CO})_{10}$ .



40  
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41  
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The complex  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  is the first example of a carbonyl bridge between two rhenium atoms and one of the few examples of carbonyl bridges across third-row transition metals. Other carbonyl bridges between third-row transition metals are known only for  $\text{Os}_2(\text{CO})_9$ <sup>173,174</sup> and  $\text{Pt}_4(\text{CO})_5(\text{PPh}_3)_4$ <sup>179</sup>. Metal-metal bonds supported by a single carbonyl are also rare and other known examples are  $\text{Os}_2(\text{CO})_9$ ,  $\text{Ru}_2(\text{CO})_9$ ,<sup>173,174</sup>  $\text{Cp}_2\text{Rh}_2(\text{CO})_3$ ,<sup>175</sup> and  $\text{Cp}_2\text{V}_2(\text{CO})_5$ .<sup>180</sup>

Irradiations on the manganese complex  $\text{CpMn}(\text{CO})_3$  have been carried out in this laboratory<sup>181</sup> but no support for the formation of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  was obtained. However, some evidence for the oligomers  $[\text{CpMn}(\text{CO})_2]_n$  ( $n = 2, 3$ ) was obtained. These oligomers were also observed in the decomposition of  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$ . The preparation and properties of the latter compound and related species will now be discussed in the following section.



## B. Silicon Derivatives of $\text{CpMn}(\text{CO})_3$ and $\text{CpRe}(\text{CO})_3$ .

### Introduction

Chapters III and IV have described the synthesis and properties of some silicon dinuclear-transition-metal hydrides. This section will relate the preparation and properties of various silicon mononuclear-metal hydrides of the type  $\text{R}_3\text{SiHM}(\text{CO})_2\text{Cp}$  ( $\text{M} = \text{Mn}, \text{Re}$ ) and of some related complexes.

The X-ray structure determination of  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  (prepared in the present work) by Bennett and Hutcheon<sup>182</sup> intensified interest in complexes of this type. The structure determination unambiguously located the unique hydride ligand at a normal covalent bond distance from the manganese atom (1.62 Å) but close enough to the silicon atom (1.76 Å) to imply some degree of bonding interaction. This appeared to be a simple example of the silicon-hydrogen-transition metal bridges suggested for the dinuclear rhenium and tungsten derivatives in Chapter III. Thus other compounds related to the manganese compound were synthesized and studied to discern any features characteristic of 'bridging' hydrogens. However, as stated in Chapter III, no clear-cut features emerged which can readily distinguish bridged and non-bridged hydrogens.

This section will also describe the deprotonation of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ . Reprotonation led to the isolation of the

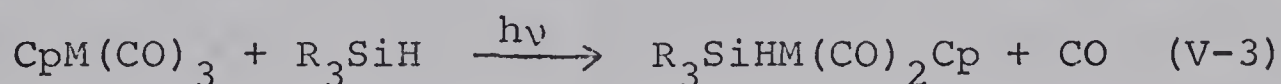


trans form of the original complex. Other reactions of the anion  $[\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}]^-$  are also described.

## Results and Discussion

### 1. Synthesis and Chemical Properties.

The silyl metal hydrides  $\text{R}_3\text{SiHM}(\text{CO})_2\text{Cp}$  were prepared by ultraviolet irradiation of the appropriate tricarbonyl with the necessary silane in benzene or hexane solution.



For  $\text{M} = \text{Mn}$ ,  $\text{R}_3\text{SiH} = \text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$

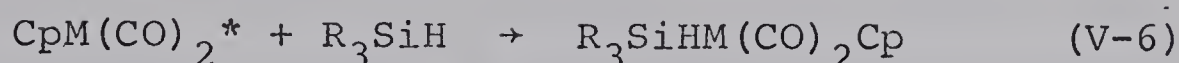
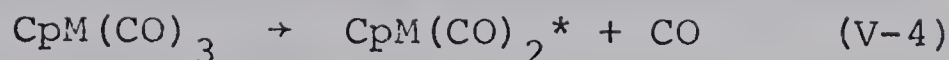
For  $\text{M} = \text{Re}$ ,  $\text{R}_3\text{SiH} = \text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$ ,  $(\text{PhCH}_2)_3\text{SiH}$

As mentioned previously similar mononuclear silylhydride derivatives of manganese, chromium, iron, cobalt and rhodium have been synthesized in this laboratory by employing the same method.<sup>66,67,183</sup>

A reasonable first step for the reactions of equation V-3 appears to be formation of the intermediate  $\text{CpM}(\text{CO})_2^*$  (V-4), which in subsequent steps may recombine with CO to form starting tricarbonyl (V-5), combine with the silane to form the observed product (V-6), or combine with a molecule of the tricarbonyl to form the dinuclear species  $\text{Cp}_2\text{M}_2(\text{CO})_5$  (V-2). In these silane reactions excess silane was employed to ensure that equation V-6 was the dominant one.

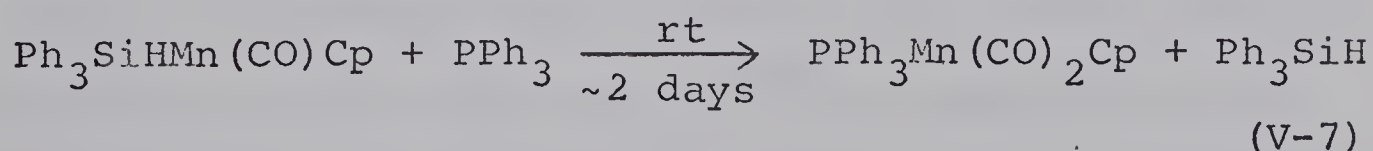






Both the manganese and rhenium derivatives are moderately air-stable crystalline solids in the pure state. However, slight variations in work-up procedures were required between the manganese and rhenium compounds. The manganese derivatives  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  and  $\text{Ph}_2\text{SiH}_2\text{Mn}(\text{CO})_2\text{Cp}$  were easily purified by recrystallizations. However, the rhenium analogs were obtained in pure crystalline form only by chromatography followed by repeated crystallizations. Since the rhenium complexes are more stable than the manganese ones, little decomposition occurred during chromatography.

The manganese complexes  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  and  $\text{Ph}_2\text{SiH}_2\text{Mn}(\text{CO})_2\text{Cp}$  reacted smoothly with triphenylphosphine to eliminate  $\text{Ph}_3\text{SiH}$  and  $\text{Ph}_2\text{SiH}_2$  respectively.



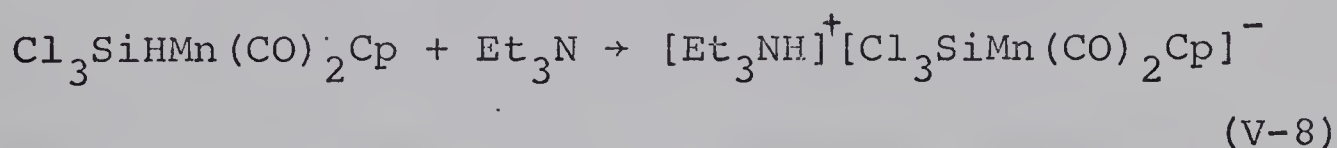
The rhenium analogs reacted much more slowly but appeared to give the same reaction. A study of the kinetics and mechanism of reaction V-7 in this laboratory showed that the results were consistent with a concerted single-step silane dissociation.<sup>151</sup> This result is compatible with the silicon-





hydrogen interaction as found in the solid-state crystal structure of  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$ .<sup>182</sup> The exact location of the hydride ligand in the rhenium analogs is not known; this aspect is discussed further in the spectroscopic section.

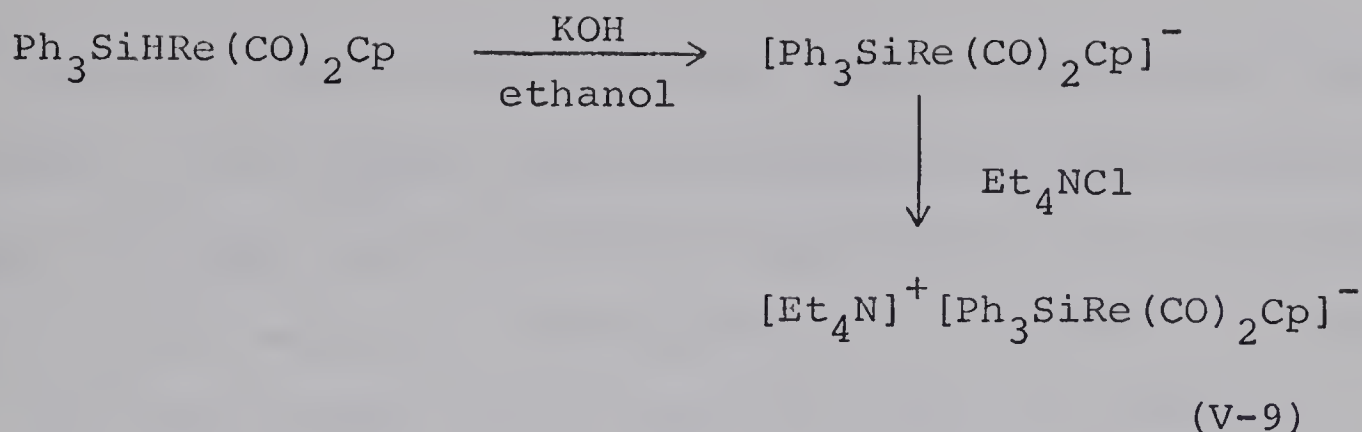
It has been shown that silyl transition-metal hydrides,<sup>184</sup> like transition-metal hydrides in general, cover a wide range of acidities. In the silyl compounds the acidities are greatly affected by the substituents on the silicon. For example,  $\text{Cl}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  can be deprotonated to produce the triethylammonium salt.<sup>184</sup>



However, the phenyl analog  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  gave no observable reaction under the same conditions. The rhenium analogs described here showed the same behaviour; deprotonation of  $\text{Cl}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  was effected with  $\text{Et}_3\text{N}$  while no reaction occurred with  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ .

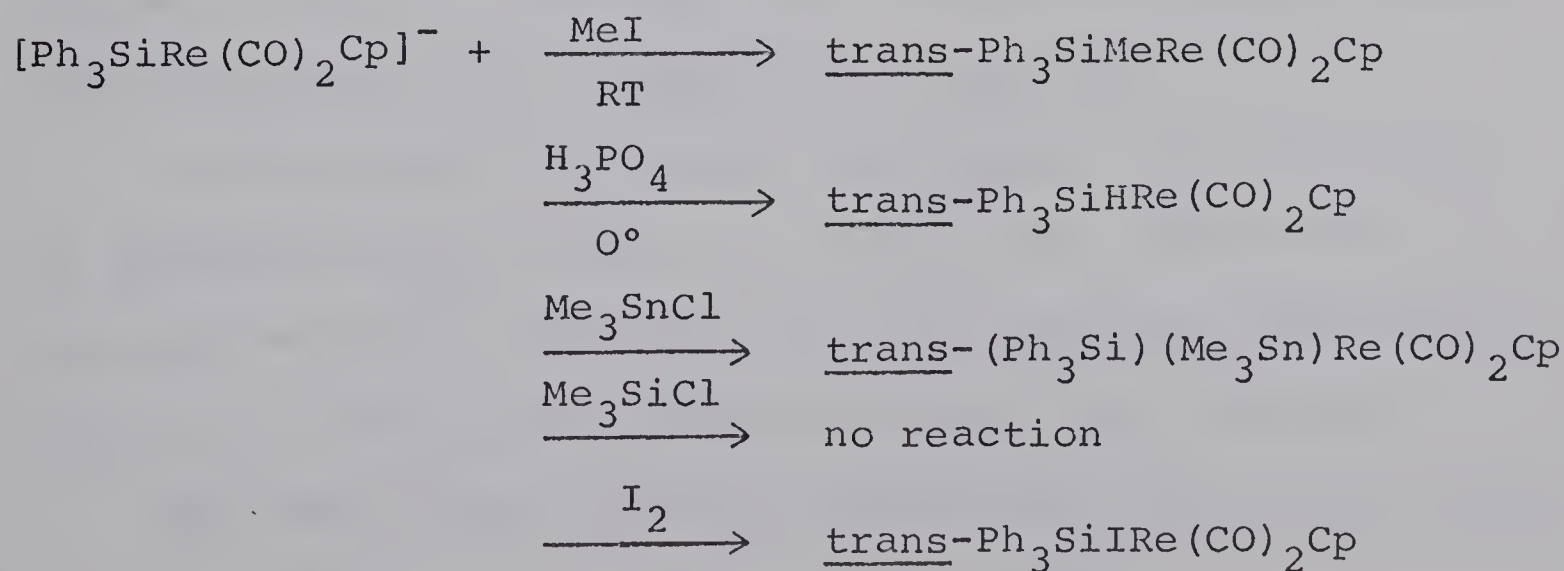
Using the stronger base ethanolic KOH, which has been successfully used by Kaesz et al.<sup>106</sup> to deprotonate the rhenium hydride  $[\text{HRe}(\text{CO})_4]_3$ , the complex  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  was deprotonated and isolated as the tetramethylammonium salt  $[\text{Et}_4\text{N}]^+[\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$ , a moderately air-stable crystalline solid. However, attempted deprotonation of the manganese complex  $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  with ethanolic KOH gave no isolable product.





Very recently Ruff<sup>185</sup> has reported the preparation of the similar tin and germanium anions  $[\text{Cl}_3\text{SnMn}(\text{CO})_2\text{Cp}]^-$  and  $[\text{Cl}_3\text{GeMn}(\text{CO})_2\text{Cp}]^-$  by the ultraviolet irradiation of  $\text{CpMn}(\text{CO})_3$  in the presence of  $[\text{Cl}_3\text{Sn}]^-$  or  $[\text{Cl}_3\text{Ge}]^-$ .

Preliminary examination of the reactions of  $[\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  showed that it undergoes metathetical reactions similar to the established carbonylate anions such as  $[\text{Mn}(\text{CO})_5]^-$  and  $[\text{Re}(\text{CO})_5]^-$ . Other silyl carbonylate anions such as  $[\text{Me}_3\text{SiRu}(\text{CO})_4]^-$ <sup>186</sup> and  $[\text{Cl}_3\text{SiFe}(\text{CO})_4]^-$ <sup>184</sup> have also been found to undergo similar reactions. The reactions of  $[\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  which were carried out in the present work are summarized in the following scheme.





The most interesting aspect of these reactions is the formation of the trans isomer of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  (assignment of cis and trans configuration is discussed in the following spectroscopic section). Protonation of the anion at  $0^\circ$  gave only the trans isomer; this isomer can then be converted cleanly to the cis form by heating in hexane solution at  $70^\circ$  for ten hours. At room temperature this trans  $\rightarrow$  cis conversion was slower and some trans was present even after long periods in solution (3-4 weeks). This suggests that at room temperature in solution an equilibrium exists between cis and trans forms, with cis dominant. Both isomers can be obtained pure in the solid state and no isomerization seems to occur in the solid. In the photochemical preparation of cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ , infrared bands were observed (in low concentrations) which can now be assigned to the trans isomer. A similar cis-trans isomerism has been observed for tungsten and molybdenum complexes of the type  $\text{XYM}(\text{CO})_2\text{Cp}$ <sup>187</sup> ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{phosphine or phosphite}$ ;  $\text{Y} = \text{halogen, alkyl, or hydrogen}$ ) and a detailed study of these interconversions has recently been reported.<sup>188</sup>

Triethylamine accelerated the trans  $\rightarrow$  cis conversion of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ ; after one hour at room temperature an n-hexane solution containing  $\text{Et}_3\text{N}$  and trans- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  appeared to form an equilibrium mixture (cis dominant).

The other anion reaction derivatives given in the above





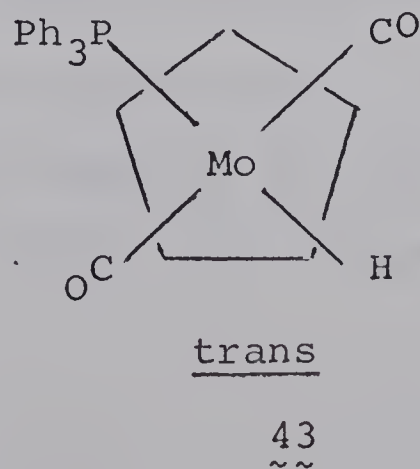
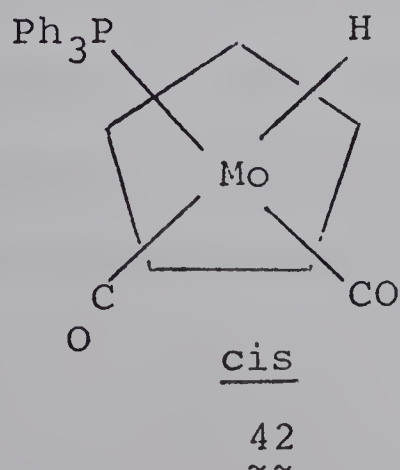
scheme have bulkier ligands ( $\text{Me}$ ,  $\text{I}$ ,  $\text{Me}_3\text{Sn}$ ) than the hydride and thus were stable in the trans form. No conversion to cis was observed even on heating up to  $100^\circ$ .

The failure of  $\text{Me}_3\text{SiCl}$  to react with  $[\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  is a further indication of the unsuitability of anion displacement reactions for forming silicon-transition metal bonds; this was noted previously in Chapter II.

## 2. Spectroscopic Properties and Structure

### Infrared Spectra

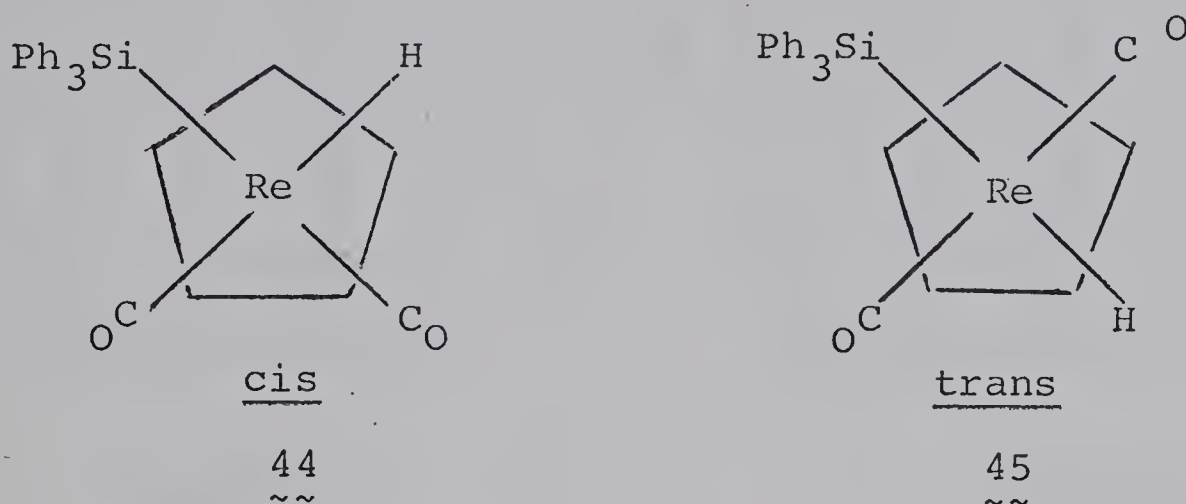
The assignment of cis or trans configuration for the complexes of type  $\text{XYM}(\text{CO})_2\text{Cp}$  is based mainly on infrared, namely the relative intensities of the carbonyl stretching bands. These complexes may be regarded as distorted square pyramidal structures with the cyclopentadienyl ring at the apical position.<sup>188</sup> Compounds showing a more intense high energy carbonyl stretching band were assigned as the cis-isomer and the ones with more intense low energy bands were assigned as trans by previous workers<sup>189,190,191</sup> for the tungsten and molybdenum derivatives. The cis and trans isomers for  $\text{PPh}_3\text{HMo}(\text{CO})_2\text{Cp}$  are shown in 42 and 43.







The rhenium and manganese compounds described here are structurally related to the molybdenum and tungsten compounds described above and thus cis and trans isomers can be assigned analogously; however, the compounds are chemically quite different. The two possible structures for the compound  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  are shown in 44 and 45.



Figures 42-49 show infrared spectra in the carbonyl stretching region of the various manganese and rhenium complexes; the appropriate cis or trans assignments are given. The X-ray structure determination of cis- $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  gives support to the assignment; the structure is shown in Figure 50.

The cis and trans forms of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  showed different carbonyl stretching frequencies besides the differences in relative band intensities (see Table XVII). These differences in frequencies were not observed for the molybdenum and tungsten complexes,<sup>187,188</sup> where only changes in



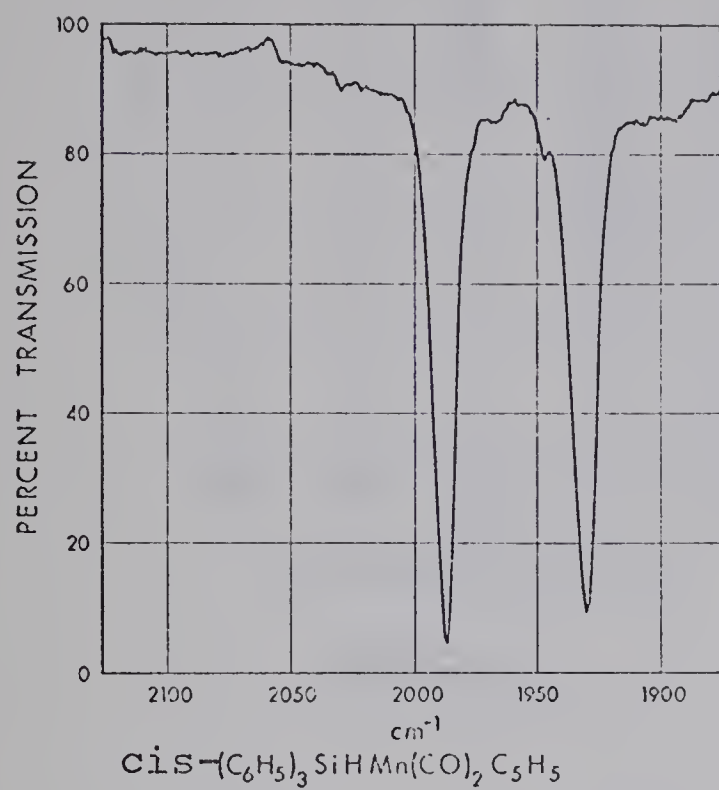


FIGURE 42

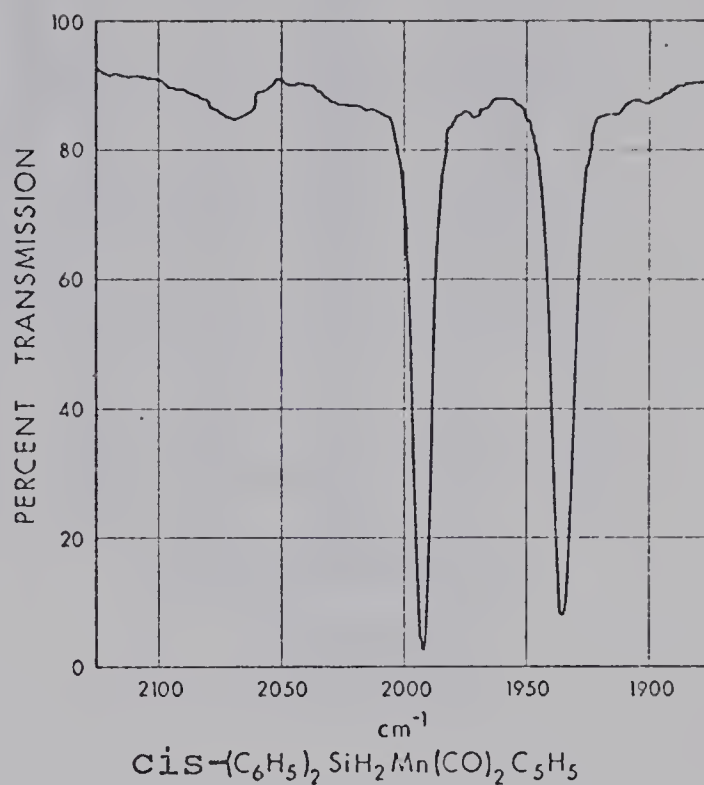


FIGURE 43

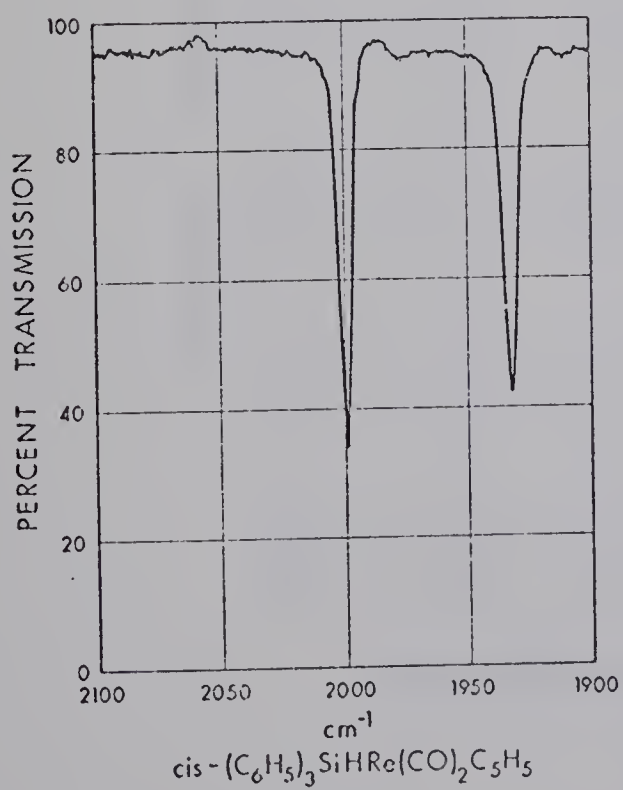


FIGURE 44

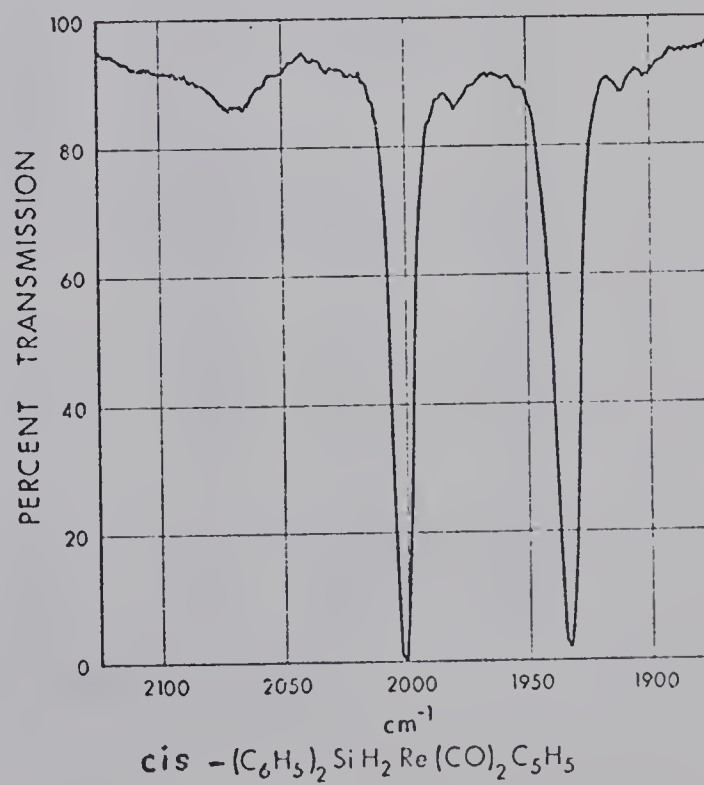


FIGURE 45



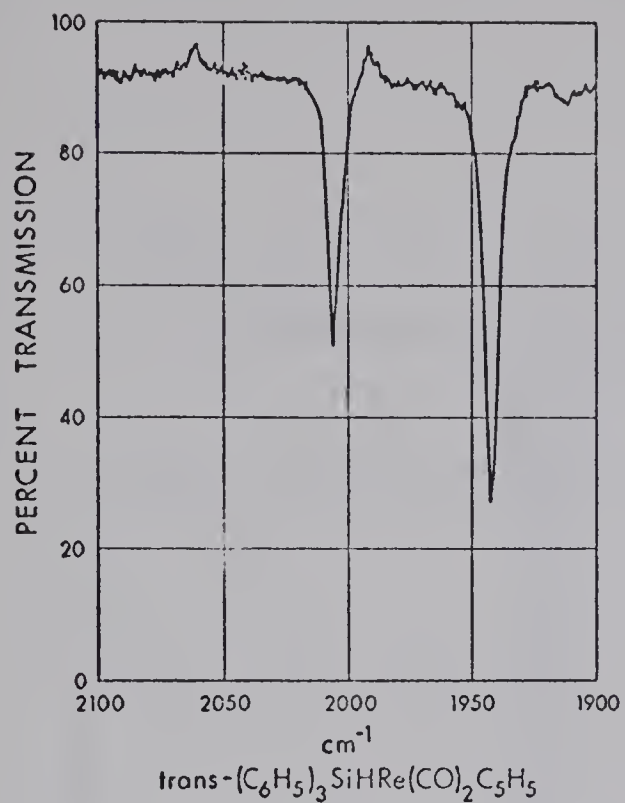


FIGURE 46

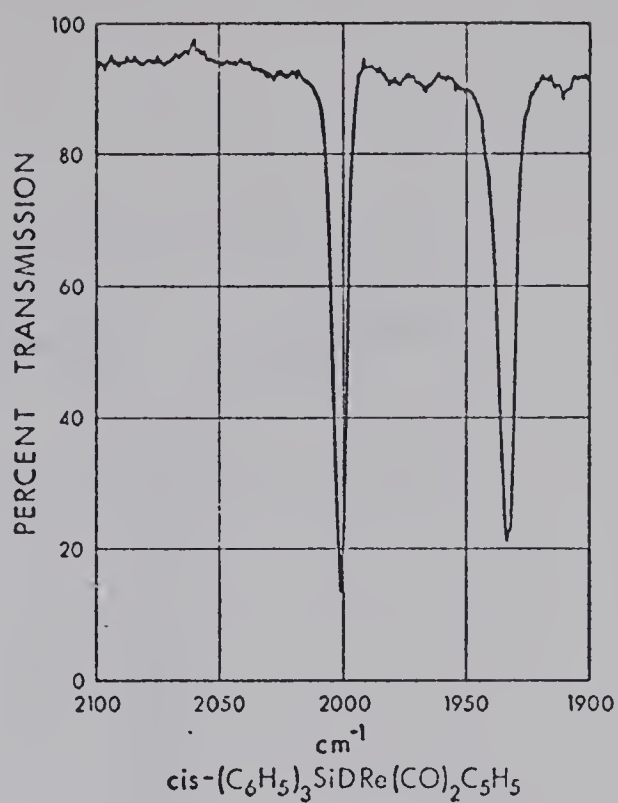


FIGURE 47

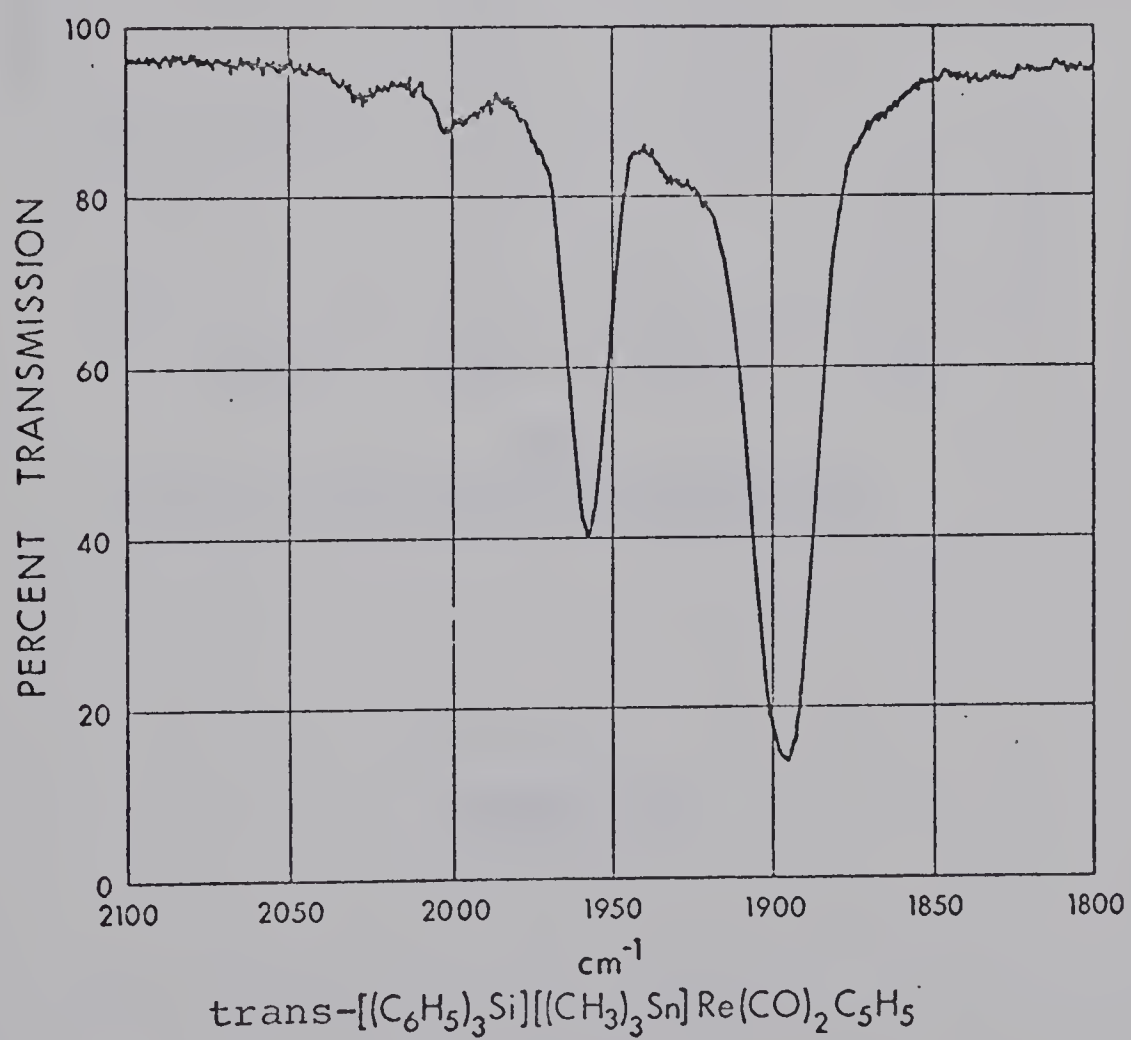
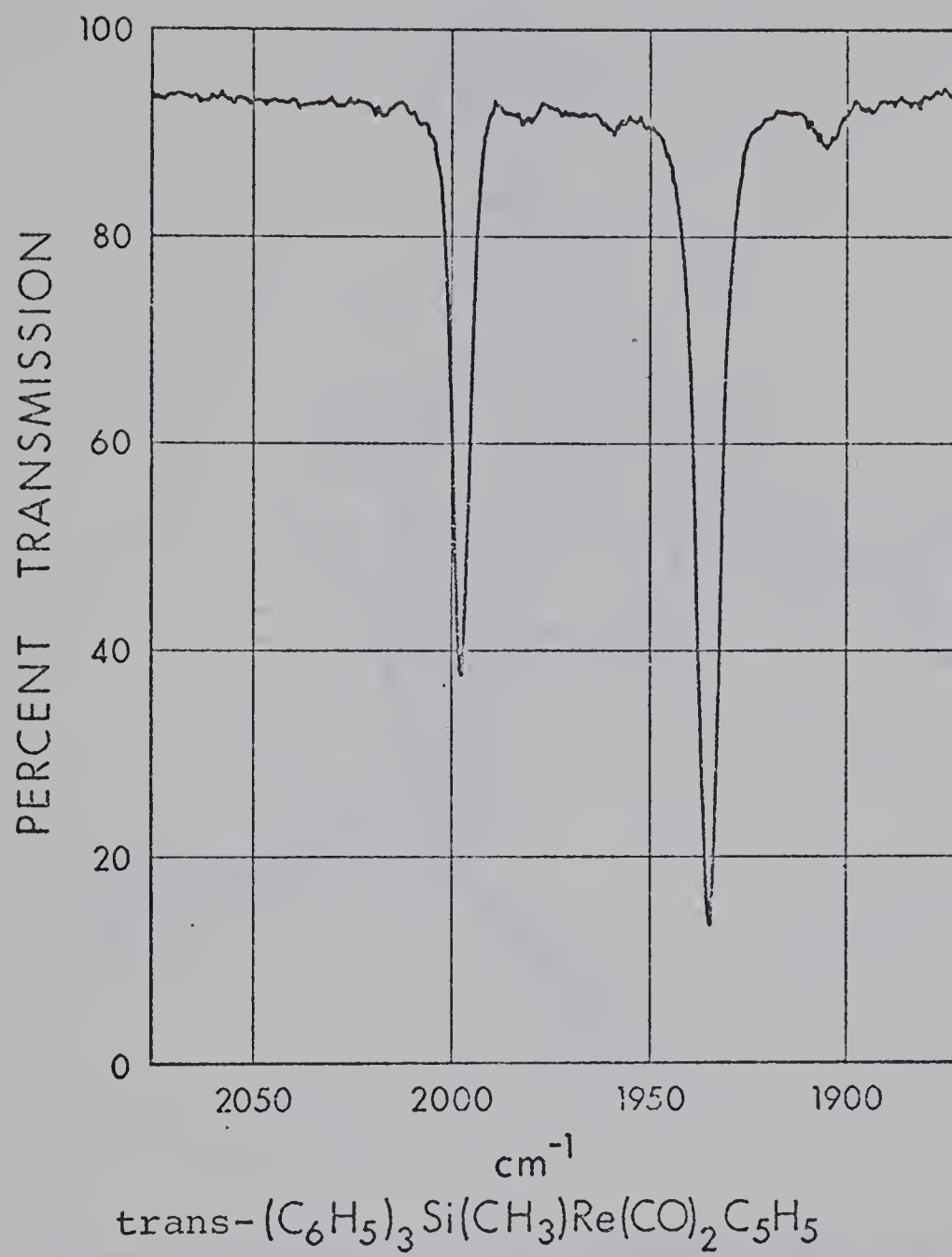


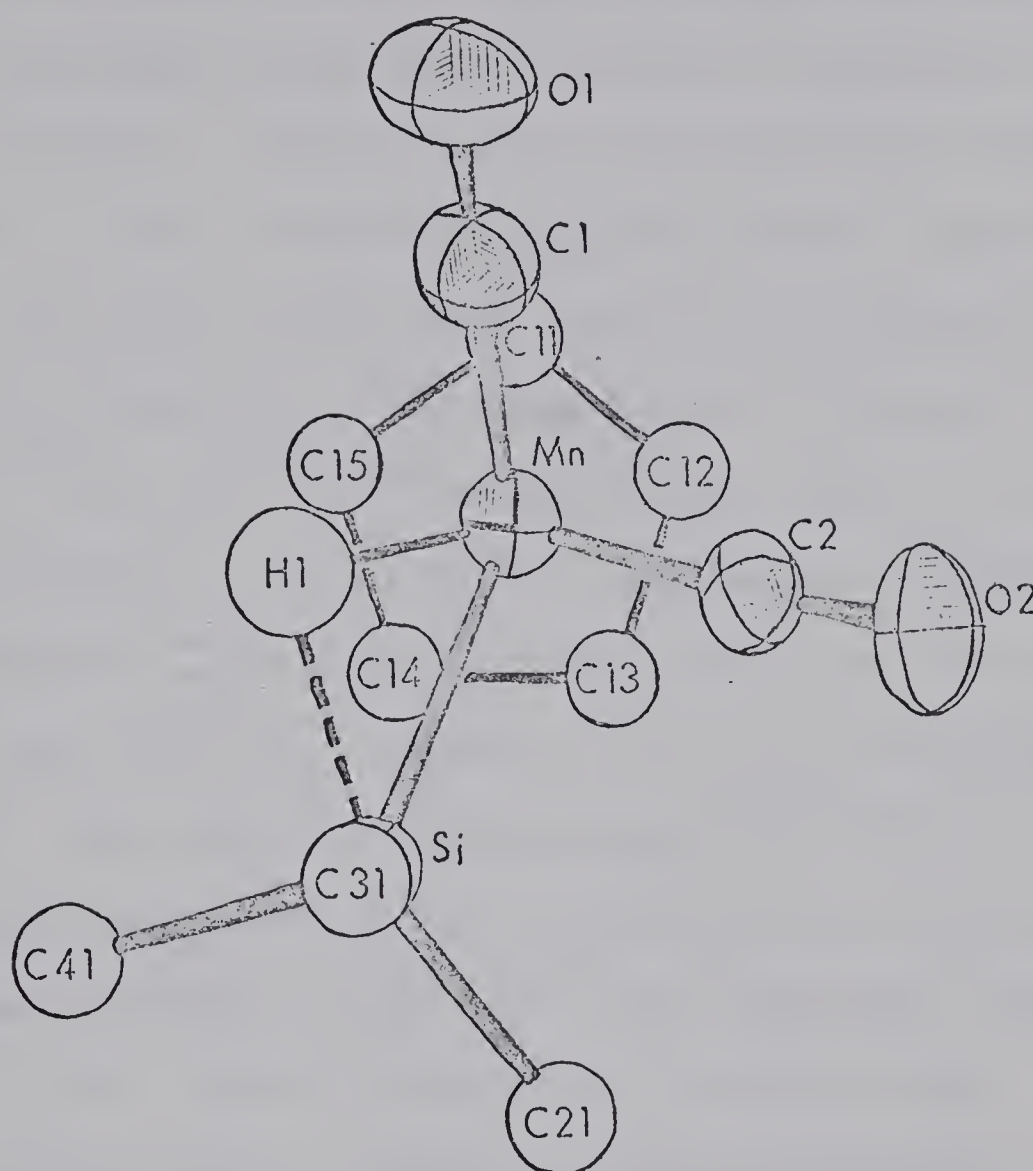
FIGURE 48



FIGURE 49







Molecular Structure of cis-Ph<sub>3</sub>SiHMn(CO)<sub>2</sub>Cp <sup>182</sup>

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FIGURE 50

relative band intensities were observed. However, different nmr chemical shifts were observed for the cis and trans isomers of the molybdenum and tungsten derivatives as is the case for the rhenium compounds described here.



Resembling the dinuclear hydrides of Chapters III and IV, the mononuclear hydrides  $R_3SiHM(CO)_2Cp$  described here showed no infrared bands which could be ascribed to M-H stretching modes. However, Raman spectroscopy located these frequencies in the 'normal' terminal hydride stretching region. The solid-state Raman spectra of cis- $Ph_3SiMn(CO)_2Cp$  and cis- $Ph_3SiDMn(CO)_2Cp$ <sup>151</sup> showed Mn-H and Mn-D frequencies at  $1900\text{ cm}^{-1}$  and  $1355\text{ cm}^{-1}$  respectively ( $\nu_H/\nu_D = 1.40$ ).<sup>115</sup>

The closely related chloro complexes  $Cl_3SiHMn(CO)_2Cp$  and  $Cl_3SiDMn(CO)_2Cp$  showed hydride and deuteride modes at  $1887\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  ( $\nu_H/\nu_D = 1.39$ ) in the infrared spectra.<sup>66</sup> The rhenium complexes cis- $Ph_3SiHRe(CO)_2Cp$  and cis- $Ph_3SiDRe(CO)_2Cp$  showed the hydrogen and deuterium modes in the Raman spectra at  $2013\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$  respectively ( $\nu_H/\nu_D = 1.40$ ). Of the complexes discussed only cis- $Ph_3SiHMn(CO)_2Cp$  is known to have the hydride ligand located in a bridging position. As discussed in Chapter III for the dinuclear complexes, one cannot say from the evidence presently available whether the hydrogens in the other complexes are bridging or not.

Other infrared features of the cyclopentadienyl manganese and rhenium complexes can be noted. The complexes cis- $Ph_2SiH_2Mn(CO)_2Cp$  and cis- $Ph_2SiH_2Re(CO)_2Cp$  showed weak, broad bands at ca.  $2070\text{ cm}^{-1}$  (Figures 43 and 45) which can be assigned to the terminal Si-H stretching modes. The infrared spectrum of trans-( $PhCH_2$ )<sub>3</sub> $SiMeRe(CO)_2Cp$  showed 'extra'



carbonyl bands (Figure 51) which may be ascribed to 'conformational effects' similar to those described in Chapter VI.

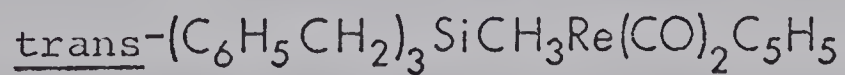
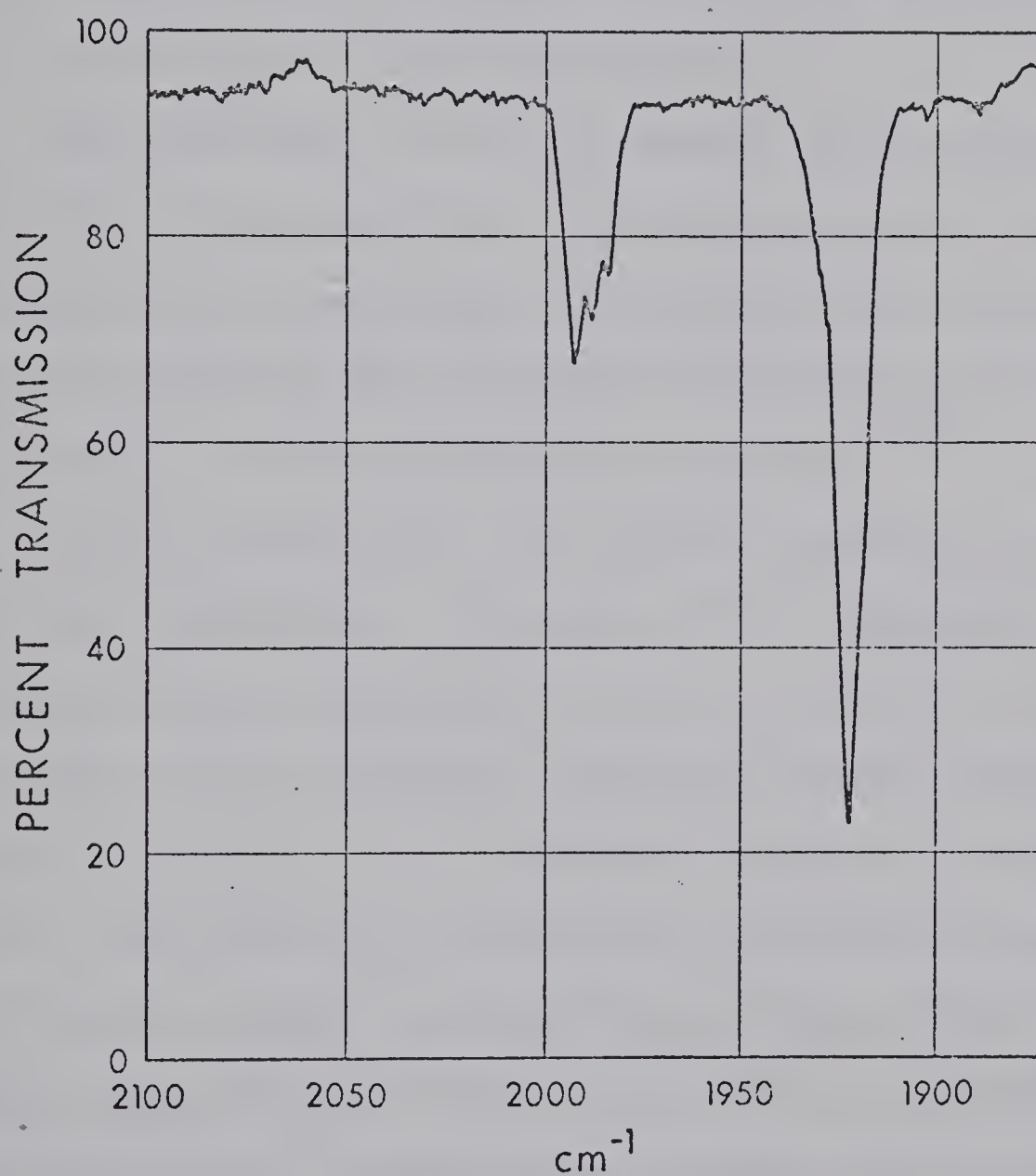


FIGURE 51



## Nmr Spectra

The hydride complexes  $R_3SiHM(CO)_2Cp$  all showed high-field nmr resonances in the  $\tau$  19-22 region (Table XVII). These chemical shifts are very similar to those of the silyl (dinuclear-metal) hydrides of Chapter III and also to mononuclear derivatives of other transition metals which have been synthesized in this laboratory.<sup>66</sup>

The manganese complexes showed broad resonances for both the cyclopentadienyl and hydride protons and so any couplings of less than ca. 5 Hz could not be discerned. This was probably due to slight dissociation or decomposition in solution to form paramagnetic species.<sup>181</sup>

On the other hand the rhenium complexes showed very sharp nmr resonances. The high-field resonance in cis- $Ph_2SiH_2Re(CO)_2Cp$  appeared as a 1:1 doublet ( $J = 2.7$  Hz), the splitting due to coupling with the terminal hydrogen on the silicon ( $\tau$  4.03). A H-H coupling constant for  $Ph_2SiH_2$  itself was not available so a comparison could not be made such as was done for  $Me_2SiH_2$  and  $Me_2SiH_2Re_2(CO)_8$  (Chapter III). The complex cis-( $PhCH_2$ )<sub>3</sub> $SiHRe(CO)_2Cp$  might be expected to show coupling between the methylene protons and the hydride proton if the hydride ligand was proximate to the silicon; however, no coupling was detected. Attempts were made to find coupling between the hydride and  $Si^{29}$  (spin =  $\frac{1}{2}$ , 4.7% natural abundance) in the complex cis- $Ph_3SiHRe(CO)_2Cp$  by CAT scans of the hydride region; however, no observable couplings







were found. The cyclopentadienyl resonances of the rhenium hydrides all appeared as sharp singlets; this can be contrasted to the complexes  $\text{Cp}_2\text{ReH}$  and  $[\text{Cp}_2\text{ReH}_2]^+$  where the cyclopentadienyl protons were coupled to the hydride protons with  $J = 1.0$  and  $0.56$  Hz respectively.<sup>192</sup>

Although of some interest, the above nmr data appear to give little insight into the nature of the hydride ligands.

### Mass Spectra

As described previously mass spectrometry was one of the essential techniques in characterizing the complexes. Molecular ions were observed for all of the neutral complexes listed in Table XVII. The manganese and rhenium hydride complexes showed the molecular ions with little or no hydride loss; the possible implications of this to a hydrogen bridged structure have been given previously.

The fragmentations of cis- $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  and cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  showed some clear differences. The mass spectrum of cis- $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  was essentially that of triphenylsilane showing a very strong  $[\text{Ph}_3\text{SiH}]^+$  peak. The parent ion  $[\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}]^+$  and the peaks corresponding to the loss of two carbonyls were very weak or unobservable. This facile elimination of triphenylsilane is consistent with the bridging interaction and with the displacement of triphenylsilane with triphenylphosphine as previously argued. The mass spectrum of  $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  differs from the manganese analog



in that the silane fragment appears mainly as  $[\text{Ph}_3\text{Si}]^+$  rather than  $[\text{Ph}_3\text{SiH}]^+$ . This implies a less facile elimination of silane than for the manganese complex as kinetic studies have also shown;<sup>151</sup> however, triphenylsilane was eliminated, although much more slowly, when reacted with triphenylphosphine. The only inference one can make is that  $\text{Ph}_3\text{SiH}$  is held more firmly in cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  than in cis- $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$ .

### Summary

The chemical and spectroscopic evidence indicate support for the bridging location of the unique hydrogen in cis- $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$  as found in the structure determination. The structure determinations of cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  and related compounds are currently under investigation in this department and may shed more light on the essence of the hydride ligands.<sup>163</sup> The variations in the spectroscopic properties suggest that there may be varying degrees of silicon-hydrogen interactions. The main bonding interaction, however, is considered to be between the transition metal and hydrogen in all cases.



## E X P E R I M E N T A L

### General Procedure and Apparatus

A nitrogen atmosphere was maintained during all reactions and during work-up procedures mainly by the use of Schlenk apparatus. Ultraviolet irradiations were performed using equipment and procedures described in Chapter III.

Melting points, microanalyses, infrared spectra, nmr and mass spectra were obtained as previously described. The results are given in Tables XVI and XVII.

Chemicals, solvents and other materials were the same as described before. Samples of  $\text{CpMn(CO)}_3$  were purchased from Alfa Inorganics.

### Procedures

#### $(\pi\text{-Cyclopentadienyl})\text{tricarbonylrhenium}, \text{CpRe(CO)}_3$

Samples of this compound were prepared by using a slight modification of the procedure given by Green and Wilkinson.<sup>194</sup> A typical preparation follows. A mixture of rhenium carbonyl (8.5 g, 13 mmol) and 50 ml dicyclopentadiene was refluxed (190-195°) for 20 hours. Cooling of the reaction solution resulted in a pale-brown paste. Extraction of this paste with 350 ml n-hexane and cooling to -20° gave a pale-yellow solid. Sublimation at 50° (0.01 mm) afforded white crystals (5.8 g, 65%) of the product  $\text{CpRe(CO)}_3$ .





TABLE XVI

COLORS, MELTING POINTS, AND ANALYTICAL DATA OF  $\text{CpRe}(\text{CO})_3$  and  $\text{CpMn}(\text{CO})_3$  DERIVATIVES

Compound	Color	Mp	Calculated %		Found %	
			$\underline{\text{C}}$	$\underline{\text{H}}$	$\underline{\text{C}}$	$\underline{\text{H}}$
$\text{Cp}_2\text{Re}_2(\text{CO})_5$	yellow	138-140 dec	28.05	1.57	27.98	1.65
<u>cis</u> - $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$	yellow	111-112 dec	68.79	4.85	68.68	4.89
<u>cis</u> - $\text{Ph}_2\text{SiH}_2\text{Mn}(\text{CO})_2\text{Cp}$	white	74-75	63.31	4.76	63.04	4.92
<u>cis</u> - $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$	white	151-153	52.89	3.73	52.54	3.75
<u>cis</u> - $\text{Ph}_2\text{SiH}_2\text{Re}(\text{CO})_2\text{Cp}$	white	103-105	46.41	3.49	46.53	3.77
<u>trans</u> - $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$	white	123-125	52.89	3.73	52.58	3.91
$(\text{PhCH}_2)_3\text{SiHRe}(\text{CO})_2\text{Cp}$	pale yellow	>130 dec	55.14	4.46	55.14	4.51
$[\text{Et}_4\text{N}]^+[\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$	pale yellow	>140 dec	56.87	4.03	55.95	4.94
<u>trans</u> -( $\text{Ph}_3\text{Si}$ ) $\text{MeRe}(\text{CO})_2\text{Cp}$	white	185-187	53.68	3.98	54.57	3.75
<u>trans</u> -( $\text{Ph}_3\text{Si}$ )( $\text{Me}_3\text{Sn}$ ) $\text{Re}(\text{CO})_2\text{Cp}$	white	158-160 dec	46.04	4.01	46.10	4.20
<u>trans</u> - $\text{Ph}_3\text{SiIRe}(\text{CO})_2\text{Cp}$	yellow	150-152	43.29	2.91	43.60	3.05
<u>trans</u> -( $\text{PhCH}_2$ ) $_3\text{SiMeRe}(\text{CO})_2\text{Cp}$	white	118-119	55.84	4.68	44.70	4.84





TABLE XVII

INFRARED CARBONYL STRETCHING FREQUENCIES AND NMR DATA FOR  $\text{CpMn}(\text{CO})_3$  and  $\text{CpRe}(\text{CO})_3$ 

## DERIVATIVES

Compound	Carbonyl Stretching Frequencies ( $\text{cm}^{-1}$ ), <sup>a</sup>	NMR Data	
		$\tau$ High-Field Proton	$\tau$ (Cp)
$\text{Cp}_2\text{Re}_2(\text{CO})_5$	1992 (0.7) 1923 (9.0) 1740 (4.5)	-	4.65
<u>cis</u> - $\text{Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$	1986 (10.0)	1929 (9.5)	21.79 ( $\text{CCl}_4$ )
<u>cis</u> - $\text{Ph}_2\text{SiH}_2\text{Mn}(\text{CO})_2\text{Cp}^b$	1991 (10.0)	1934 (9.4)	21.75 ( $\text{CCl}_4$ )
<u>cis</u> - $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$	1999 (10.0)	1932 (8.7)	19.10 ( $\text{CDCl}_3$ )
<u>cis</u> - $\text{Ph}_2\text{SiH}_2\text{Re}(\text{CO})_2\text{Cp}^c$	2001 (10.0)	1934 (9.7)	19.70 ( $\text{CDCl}_3$ ) <sup>d</sup>
<u>trans</u> - $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$	2004 (6.4)	1940 (10.0)	20.30 ( $\text{CDCl}_3$ )
$(\text{PhCH}_2)_3\text{SiHRe}(\text{CO})_2\text{Cp}$	<u>cis</u> 1995 (8.9) <u>trans</u> 1998 (6.0 sh)	1920 (10.0) 1931 (4.7)	20.59 } ( $\text{CD}_2\text{Cl}_2$ 20.63 }
$[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$	1862 (8.3)	1782 (10.0) <sup>e</sup>	5.25
<u>trans</u> - $\text{Ph}_3\text{SiMeRe}(\text{CO})_2\text{Cp}$	1995 (7.0)	1932 (10.0)	5.10
<u>trans</u> -( $\text{Ph}_3\text{Si}$ ) ( $\text{Me}_3\text{Sn}$ ) $\text{Re}(\text{CO})_2\text{Cp}$	1957 (6.8)	1898 (10.0) <sup>f</sup>	5.09
<u>cis</u> - $\text{Ph}_3\text{SiDRe}(\text{CO})_2\text{Cp}$	2000 (10.0)	1932 (9.1)	-

continued.....



TABLE XVII (continued)

<u>trans-Ph<sub>3</sub>SiDRe(CO)<sub>2</sub>Cp</u>	2003(6.6)	1940(10.0)	-
<u>trans(PhCH<sub>2</sub>)<sub>3</sub>SiMeRe(CO)<sub>2</sub>Cp</u>	1991(3.8) 1982(2.6)	1986(3.2) 1921(10.0)	-
<u>trans-Ph<sub>3</sub>SiIRe(CO)<sub>2</sub>Cp</u>	2016(6.5)	1958(10.0)	-
<u>Cl<sub>3</sub>SiHRe(CO)<sub>2</sub>Cp<sup>g</sup></u>	2033(10.0) 1968(7.8)	1977(8.0)	-

<sup>a</sup> Cyclohexane solutions. Figures in parenthesis are relative band heights on a transmittance scale; sh = shoulder, br = broad.

<sup>b</sup> Si-H stretching mode at 2073 (br) cm<sup>-1</sup>.

<sup>c</sup> Si-H stretching mode at 2070 (br) cm<sup>-1</sup>.

<sup>d</sup> Doublet with J = 2.7 Hz; silicon-bonded hydrogen doublet at τ 4.03.

<sup>e</sup> Dichloromethane solution.

<sup>f</sup> Chloroform solution.

<sup>g</sup> Characterized only by infrared and mass spectrometry.



Bis( $\pi$ -cyclopentadienyl)pentacarbonyldirhenium,  $\text{Cp}_2\text{Re}_2(\text{CO})_5$

A solution of  $\text{CpRe}(\text{CO})_3$  (0.80 g, 2.4 mmol) in 100 ml cyclohexane was irradiated with the 140 watt ultraviolet source for 2.5 hours to produce a yellow solution (a yellow solid had also precipitated). Irradiation for longer periods led only to decomposition and lower yields. Solvent was removed at reduced pressure and sublimation of the residual solid yielded 0.60 g of starting tricarbonyl. Recrystallization of the unsublimed solid from dichloromethane-n-hexane afforded yellow needles of  $\text{Cp}_2\text{Re}_2(\text{CO})_5$  (0.08 g, 10%).

Cis-hydridotriphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylmanganese,  $\text{cis-Ph}_3\text{SiHMn}(\text{CO})_2\text{Cp}$

Irradiation (140 watt source) of an n-hexane (100 ml) solution of  $\text{CpMn}(\text{CO})_3$  (0.75 g, 3.7 mmol) and triphenylsilane (2.0 g, 7.7 mmol) for 3.5 hours gave the product as a yellow microcrystalline precipitate. Filtration, washing with hexane (two times 25 ml) and drying in high vacuum afforded 0.93 g (57%) of pure product. Recrystallization from dichloromethane-hexane yielded large yellow cubes of the product (0.60 g).

Cis-hydridodiphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylmanganese,  $\text{cis-Ph}_2\text{SiH}_2\text{Mn}(\text{CO})_2\text{Cp}$

A solution of  $\text{CpMn}(\text{CO})_3$  (1.50 g, 7.4 mmol) and diphenyl-





silane (2.0 g, 10 mmol) was irradiated with the 450 watt source for one hour. Removal of solvent at reduced pressure and crystallization of the remaining oil from n-hexane gave a pale-yellow solid. Recrystallization from n-hexane afforded white crystals of cis- $\text{Ph}_2\text{SiH}_2\text{Mn}(\text{CO})_2\text{Cp}$  (0.60 g, 23%).

Cis-hydridotriphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonyl-rhenium, cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$ .

A solution of  $\text{CpRe}(\text{CO})_3$  (2.3 g, 6.9 mmol) and triphenylsilane (5.0 g, 19 mmol) in 200 ml cyclohexane was irradiated with the 450 watt source for seven hours. Reaction mixture was suction filtered through a 100 g silicic acid column (compounds absorbed on column). Elution with 300 ml n-hexane removed all of the triphenylsilane. Then the column was eluted with two 100 ml portions of 30% dichloromethane-n-hexane. The first fraction contained  $\text{CpRe}(\text{CO})_3$  (1.0 g). The second fraction contained the product and a small amount of  $\text{CpRe}(\text{CO})_3$ . Sublimation of the second fraction at 60° removed the tricarbonyl; crystallization of the unsublimed solid from dichloromethane-hexane afforded white crystals of cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  (0.55 g, 15%).

Cis-hydridodiphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonyl-rhenium, cis- $\text{Ph}_2\text{SiH}_2\text{Re}(\text{CO})_2\text{Cp}$ .





This compound was obtained from a procedure essentially identical to that described for cis-Ph<sub>3</sub>SiHRe(CO)<sub>2</sub>Cp above. Two recrystallizations were required to afford good crystals. The yield was slightly lower; one gram of CpRe(CO)<sub>3</sub> yielded 0.15 g (10%) of pure cis-Ph<sub>2</sub>SiH<sub>2</sub>Re(CO)<sub>2</sub>Cp.

Hydridotribenzylsilyl(π-cyclopentadienyl)dicarbonylrhenium,  
(PhCH<sub>2</sub>)<sub>3</sub>SiHRe(CO)<sub>2</sub>Cp.

A solution of CpRe(CO)<sub>3</sub> (0.92 g, 2.8 mmol) and tri-benzylsilane (5.0 g, 19 mmol) in 150 ml cyclohexane was irradiated (450 watt source) for six hours to give an orange-red reaction mixture. Removal of solvent at reduced pressure left an orange tar; this tar was dissolved in benzene and filtered through a short silicic acid column; evaporation of the filtrate gave a pale-yellow solid which infrared spectroscopy showed to be a mixture of starting materials and product. This mixture was sublimed at 50° to remove most of the CpRe(CO)<sub>3</sub>. The remaining solid was adsorbed onto a 20 g silicic acid column with 250 ml n-hexane. Elution with 100 ml n-hexane removed all the tribenzylsilane. Further elution with 100 ml 40% dichloromethane-n-hexane gave the product. Two recrystallizations from dichloroethane-hexane afforded pale-yellow cubes (0.60 g, 36%) of the product.



Tetraethylammonium triphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylrhenate,  $[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$

Solid cis- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$  (0.40 g, 0.70 mmol) was magnetically stirred with 5 ml of ca. 1.0 M ethanolic KOH; the hydride solid slowly dissolved and a clear yellow solution formed after 1.5 hours stirring. Addition of  $\text{Et}_4\text{NBr}$  (0.95 mmol, in 3 ml ethanol) gave an immediate pale-yellow precipitate. The mixture was centrifuged and the ethanol was decanted. The remaining solid was dried under a stream of nitrogen; crystallization from dichloromethane-hexane yielded pale-yellow prisms of the product (0.35 g, 72%).

Trans-hydridotriphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylrhenium, trans- $\text{Ph}_3\text{SiHRe}(\text{CO})_2\text{Cp}$

A solution of  $[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  (0.10 g, 0.14 mmol) in 20 ml dichloromethane was stirred vigorously with 0.5 ml phosphoric acid at  $0^\circ$  for 0.5 hours. After allowing the mixture to settle, the dichloromethane layer was decanted and evaporated at reduced pressure ( $0^\circ$ ). The white solid was recrystallized from hexane-dichloromethane to yield crystals of the pure trans product (0.06 g, 75%).

Trans-methyltriphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylrhenium, trans- $\text{Ph}_3\text{SiMeRe}(\text{CO})_2\text{Cp}$

A solution of methyl iodide (0.1 ml) and



$[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  (0.05 g, 0.07 mmol) in 15 ml dichloromethane was stirred at room temperature for 0.5 hours. After removal of solvent and excess methyl iodide at reduced pressure, recrystallization from hexane-dichloromethane (by blowing nitrogen slowly over the solution) afforded white crystals (0.03 g, 55%) of the product.

Trans-trimethyltintriphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylrhenium,  $\text{trans}-(\text{Me}_3\text{Sn})(\text{Ph}_3\text{Si})\text{Re}(\text{CO})_2\text{Cp}$ .

A solution of trimethyltin chloride (0.04 g, 0.2 mmol) and  $[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  (0.10 g, 0.14 mmol) in 25 ml dichloromethane was stirred for thirty minutes. Removal of solvent at reduced pressure and crystallization from hexane-chloroform afforded white crystals of the product (0.09 g, 70%).

Trans-iodotriphenylsilyl( $\pi$ -cyclopentadienyl)dicarbonylrhenium,  $\text{trans}-\text{Ph}_3\text{SiIRe}(\text{CO})_2\text{Cp}$

A solution of iodine (0.05 g) and  $[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SiRe}(\text{CO})_2\text{Cp}]^-$  (0.05 g, 0.07 mmol) in 10 ml dichloromethane was stirred for one hour. Removal of solvent at reduced pressure and crystallization from hexane-chloroform afforded yellow crystals of the product (0.035 g, 65%).





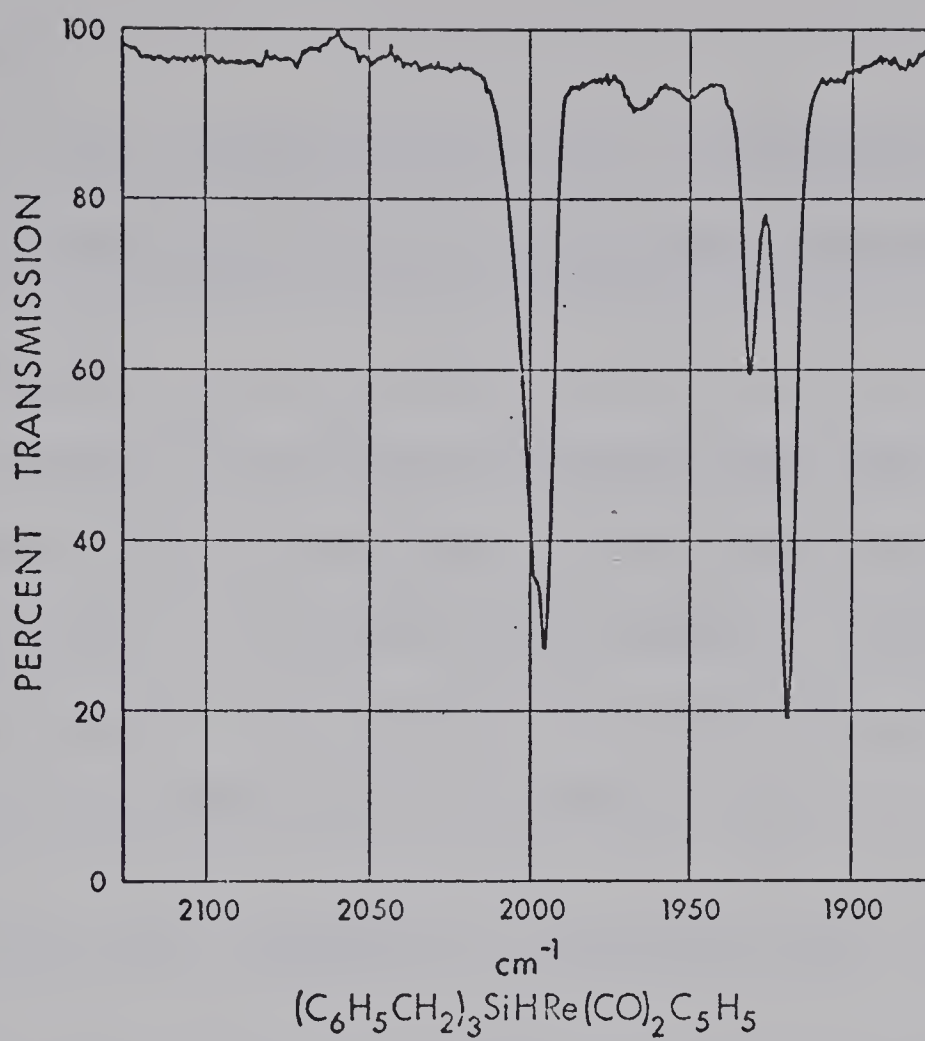


FIGURE 52

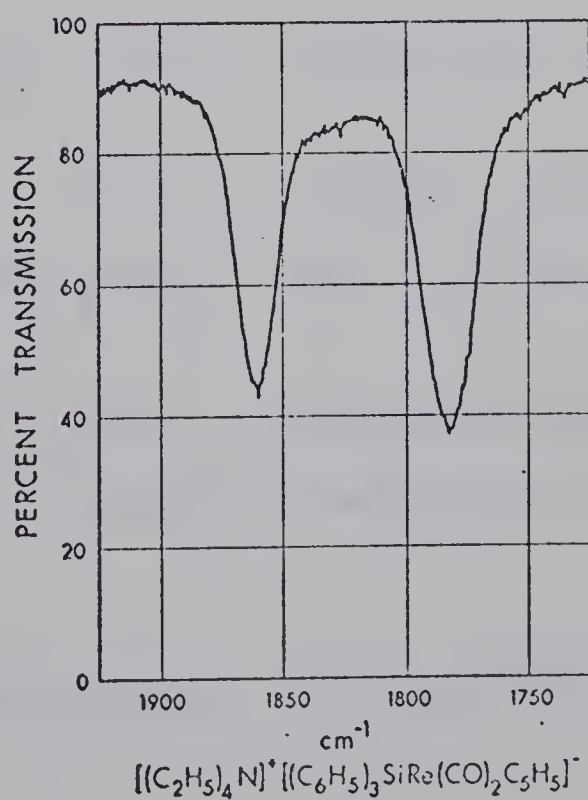


FIGURE 53



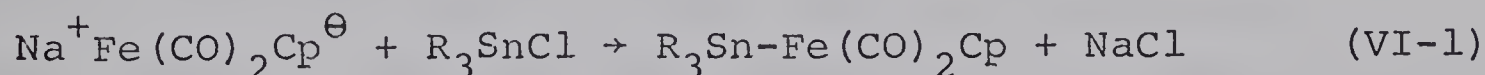


## CHAPTER VI

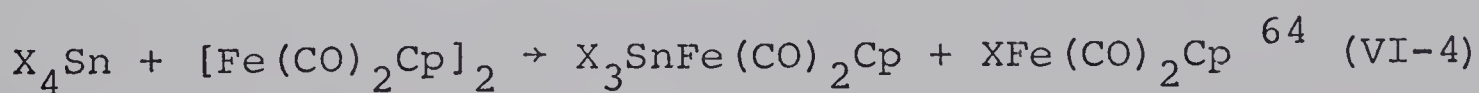
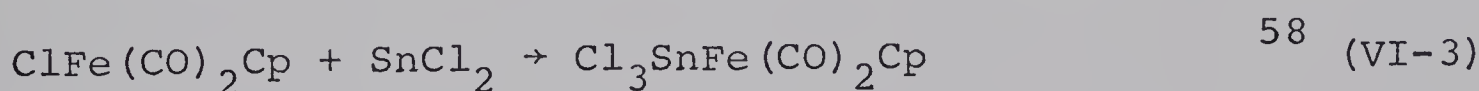
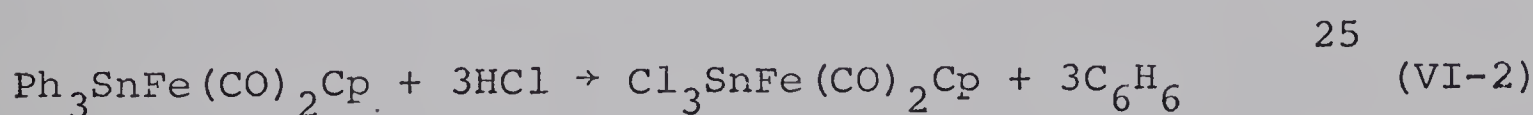
### SYNTHESIS AND PROPERTIES OF SOME $\pi$ -CYCLOPENTADIENYLDICARBONYLIRON-TIN DERIVATIVES AND RELATED COMPOUNDS.

#### Introduction

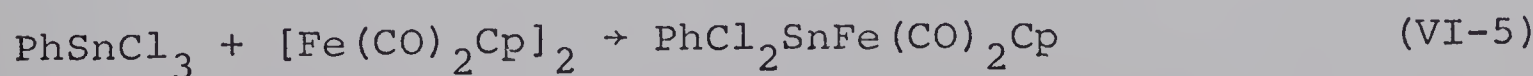
A variety of synthetic methods have been reported for the preparation of complexes of the type  $X_nR_{3-n}SnFe(CO)_2Cp$  ( $n = 0, 1, 2, 3$ ;  $X = \text{halogen}$ ;  $R = \text{alkyl or aryl}$ ). Halide displacement by the carbonylate ion  $[CpFe(CO)_2]^\ominus$ <sup>11</sup> was used to prepare the derivatives  $R_3SnFe(CO)_2Cp$  ( $R = \text{Me, Ph}$ ).<sup>25, 195</sup>



The fully halogenated derivatives have been synthesized by various routes:



The mixed derivative  $PhCl_2SnFe(CO)_2Cp$  was prepared by Edmondson and Newlands<sup>64</sup> using the method of equation (VI-4):



By extending this method (equations VI-4 and VI-5) to other



organotin halides a series of complexes of the type  $X_n R_{3-n} SnFe(CO)_2 Cp$  were synthesized and will be described in this Chapter.

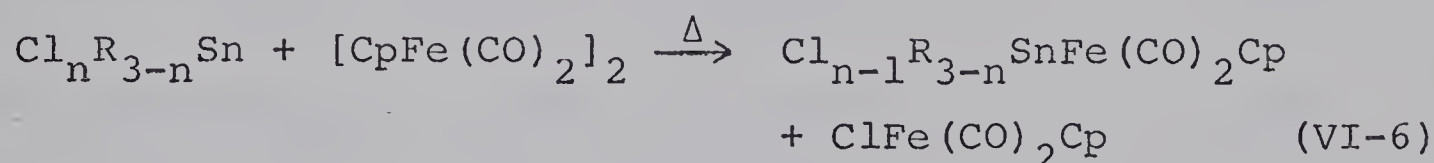
The interest in complexes of this type (where an unsymmetrical tin group is bonded to the  $Fe(CO)_2 Cp$  moiety) arose because analogous silicon derivatives such as  $MeCl_2 SiFe(CO)_2 Cp$  and  $Me_2 ClSiFe(CO)_2 Cp$  were found to show 'conformational effects' from solution infrared studies in the carbonyl stretching region.<sup>1,8</sup> Various tin analogs and similar derivatives were synthesized and the results of infrared and other spectroscopic studies will be given in this Chapter. Perfluoroalkyl derivatives  $R_F Fe(CO)_2 Cp$  which would be expected to show similar 'conformational effects' were also synthesized and examined.



## R E S U L T S   A N D   D I S C U S S I O N

### 1. Synthesis and Characterization.

The chloro derivatives,  $\text{Cl}_n\text{R}_{3-n}\text{SnFe}(\text{CO})_2\text{Cp}$  ( $n = 1, 2, 3$ ) were prepared by heating the appropriate tin chloride with  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  in an inert solvent such as cyclohexane or xylene. This procedure was first described by Newlands et al.<sup>64</sup> for the two cases mentioned above. The general course of the reactions reported here can be summarized by the following equation:



This reaction of the tin chloride with the Fe-Fe bond appears analogous to the postulated initial step in reactions of the silicon hydrides with metal-metal bonds as discussed in Chapter II.

The yields and the reaction conditions in the preparation of the chlorotin derivatives according to equation VI-6 are given in Table XVIII.

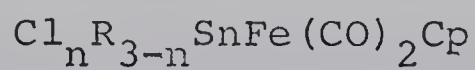
It can be seen from Table XVIII that the yields of the desired products decreased with increasing number of organic groups on the tin chloride compound. In fact, reaction of  $\text{R}_3\text{SnCl}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with  $[\text{CpFe}(\text{CO})_2]_2$  gave essentially no reaction even at temperatures up to  $160^\circ$ . However, the





TABLE XVIII

REACTION CONDITIONS AND YIELDS IN THE PREPARATIONS OF

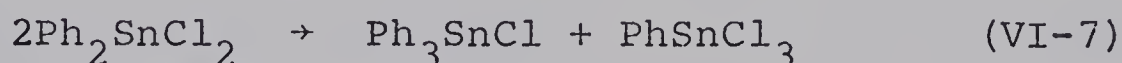


<u>Compound</u>	<u>Reaction Condition</u>	<u>Yield</u>
$\text{Cl}_3\text{SnFe}(\text{CO})_2\text{Cp}$	100° (5 hours)	55%
$\text{PhCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	100° (5 hours)	30%
$\text{MeCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	100° (15 hours)	30%
$\text{n-BuCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	65° (16 hours)	15%
$\text{Me}_2\text{ClSnFe}(\text{CO})_2\text{Cp}$	80° (20 hours)	15%



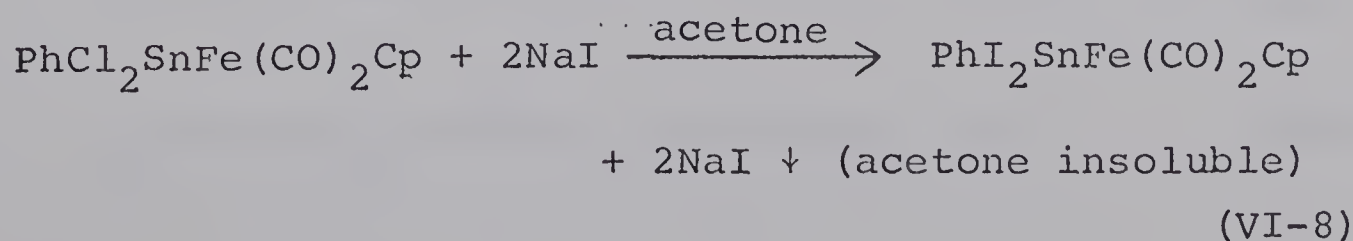
compounds  $R_3SnFe(CO)_2Cp$  ( $R = Me, Ph$ ) were obtained by using the previously reported carbonylate anion method.<sup>25,195</sup>

One compound that could not be obtained by the method of equation VI-6 was  $Ph_2ClSnFe(CO)_2Cp$ . Reaction of  $Ph_2SnCl_2$  and  $[CpFe(CO)_2]_2$  gave only a small yield of  $PhCl_2SnFe(CO)_2Cp$ . Whether this product was formed by cleavage of the phenyl-tin bond in reaction with the iron dimer  $[CpFe(CO)_2]_2$  or by redistribution of the organotin chloride (VI-7) is unknown.



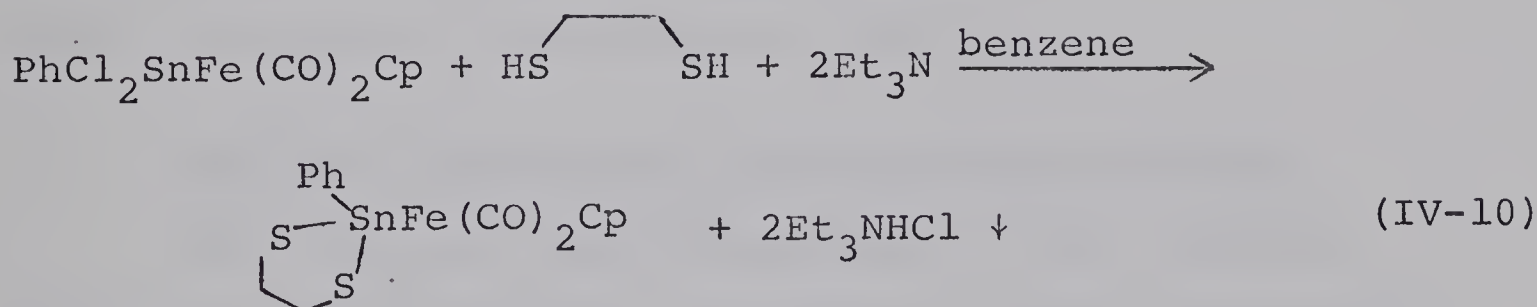
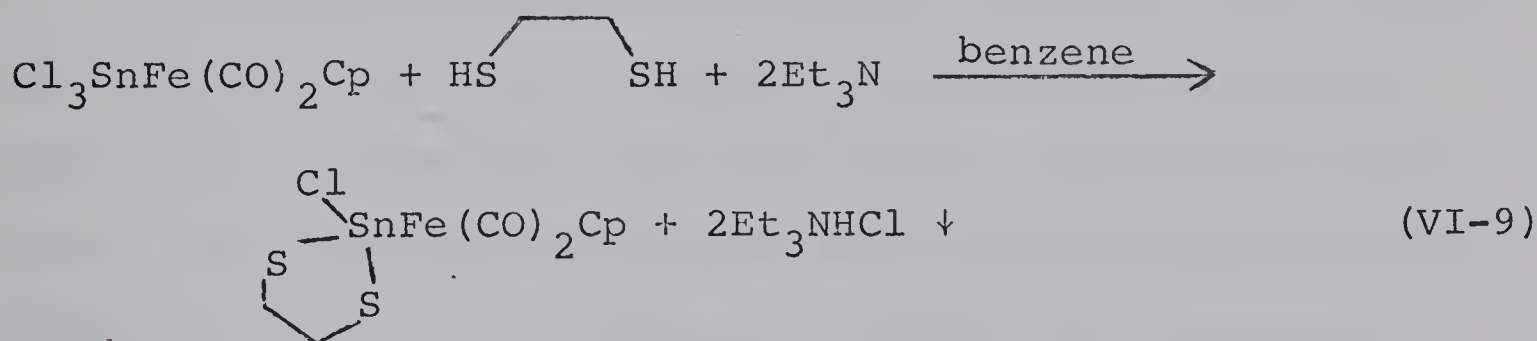
During the preparation of the compounds in Table XVIII, other products such as ferrocene and  $Cl_2Sn[Fe(CO)_2Cp]_2$  were invariably formed. This can partially be due to the fact that the reaction temperatures used were above the decomposition point of  $ClFe(CO)_2Cp$  ( $57^\circ$ ). Separation of products was accomplished mainly by chromatography on silicic acid (see Experimental for details).

The iodo-tin compounds such as  $PhI_2SnFe(CO)_2Cp$  and  $I_3SnFe(CO)_2Cp$  were obtained from the reaction of the corresponding chloride with sodium iodide in acetone solution. For example:



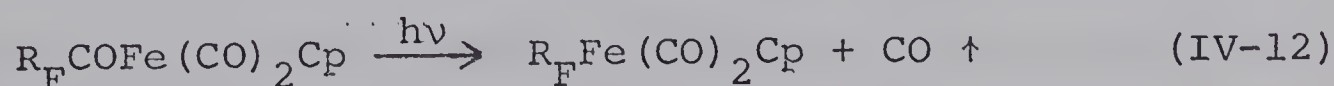
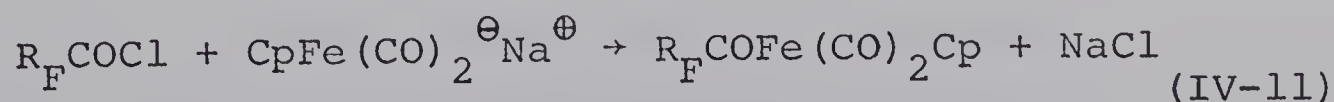


The sulfur derivatives  $(S_2C_2H_4)ClSnFe(CO)_2Cp$  and  $(S_2C_2H_4)PhSnFe(CO)_2Cp$  were prepared using the method first reported by Weber and Schmidt<sup>196</sup> for synthesizing sulfur-tin bonds. This method involves stirring of a tin halide, a thiol (RSH), and an organic base such as triethylamine all in benzene solution. The reactions proceeded as shown in (VI-9) and (VI-10).



The triethylamine hydrochloride precipitated from the benzene solution and the products were obtained in 60-90% yields.

The perfluoroalkyl and perfluoroacyl complexes were prepared as previously reported by King and Bisnette.<sup>197</sup>





The compounds described above were all moderately air-stable crystalline solids ranging in color from pale-yellow to orange (see Table XX). The compounds were soluble in chloroform, dichloromethane and benzene but only sparingly soluble in hexane or cyclohexane. However, solubility in cyclohexane was sufficient for satisfactory infrared spectra in the carbonyl stretching region.

Characterization by elemental analyses, mass spectra and solution molecular weights gave excellent agreement with calculated values (see Table XX). Especially important to the infrared discussion in the next section are the solution molecular weights which showed good agreement with a monomeric formulation in solution.

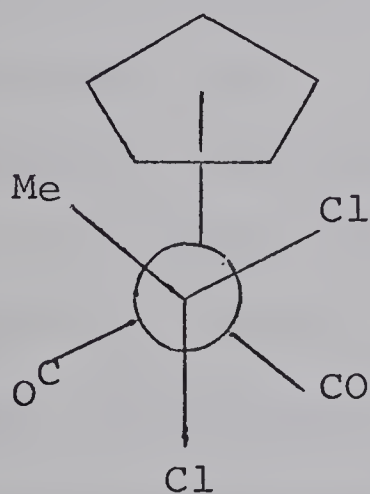
## 2. Infrared Spectra and Conformational Effects.

As stated in the introduction to this Chapter, interest in the tin-iron compounds was stimulated by the observation of 'extra' carbonyl stretching bands in the infrared spectra by Jetz and Graham<sup>1,8</sup> for analogous silicon derivatives such as  $\text{MeCl}_2\text{SiFe}(\text{CO})_2\text{Cp}$ . Only two carbonyl stretching bands (symmetric and asymmetric stretching of the carbonyls) would be expected for a complex with two carbonyl groups but four bands were observed.<sup>8</sup> This was interpreted by postulating the existence of two structurally different isomers (conformers) in solution. These can be obtained by rotation about the

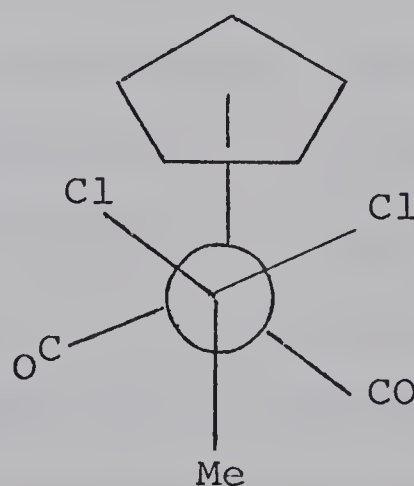




silicon-iron bond; two carbonyl bands would then be expected for each structure giving a total of four bands. The two possible isomers of  $\text{MeCl}_2\text{SiFe}(\text{CO})_2\text{Cp}$  are depicted in the Newman projections 46 and 47 looking along the iron-silicon axis. The X-ray structure of  $\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}$  has been determined by Bryan <sup>198</sup> and showed that the structure can be thought of as a trigonal pyramid with the planar cyclopentadienyl ring at the apex and the two carbonyls and the tin moiety forming the trigonal base. The silicon and other tin analogs discussed here undoubtedly have the same structure and all the interpretations given here are based on this assumption.



46  
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47  
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If the substituents on the silicon were all the same such as in  $\text{Cl}_3\text{SiFe}(\text{CO})_2\text{Cp}$  and  $\text{Me}_3\text{SiFe}(\text{CO})_2\text{Cp}$  rotation about the iron-silicon bond would give rise to structurally equivalent forms and only two carbonyl stretching bands are expected and only two were observed.<sup>8,1</sup> The



germanium compound  $\text{MeCl}_2\text{GeFe}(\text{CO})_2\text{Cp}$  has also been found to show an analogous conformational effect.<sup>199</sup>

Parallel to the silicon derivatives, the tin and perfluorocarbon derivatives prepared in this work were found to show conformational effects in the infrared. Figures 54-66 show the infrared spectra in the carbonyl stretching region for the complexes prepared (cyclohexane solution). No assignment of a particular conformer to a particular pair of bands can be made with the data available.

Some of the compounds have been reported previously and carbonyl stretching frequencies have also been reported. However, these were reported in polar solvents such as chloroform and dichloromethane which give rise to much broader bands than in hexane or cyclohexane. Therefore, resolution of the small energy differences ( $3\text{--}10\text{ cm}^{-1}$ ) found for the conformers would not be probable. At best unsymmetrical bands would be observed in polar solvents.

The differences in the energies of the carbonyl stretching frequencies between conformers appear to be dependent on the substituents on the tin. Table XIX shows the energy differences between the high energy bands ( $\Delta_1$ ) and the low energy bands ( $\Delta_2$ ) for complexes which exhibited band splittings. The magnitudes of ( $\Delta_1$ ) and ( $\Delta_2$ ) for a particular compound are similar. The general trend appears to be that the larger the electronegativity difference between the two substituents, the larger are the band splittings



TABLE XIX

CONFORMATIONAL EFFECT BAND SPLITTINGS

<u>Compound</u>	<u><math>\Delta_1</math> (cm<sup>-1</sup>)</u>	<u><math>\Delta_2</math> (cm<sup>-1</sup>)</u>
PhCl <sub>2</sub> SnFe (CO) <sub>2</sub> Cp	9	7
PhI <sub>2</sub> SnFe (CO) <sub>2</sub> Cp	7	7
MeCl <sub>2</sub> SnFe (CO) <sub>2</sub> Cp	10	7
MeI <sub>2</sub> SnFe (CO) <sub>2</sub> Cp	10	9
n-BuCl <sub>2</sub> SnFe (CO) <sub>2</sub> Cp	10	8
Me <sub>2</sub> ClSnFe (CO) <sub>2</sub> Cp	11	13
(S <sub>2</sub> C <sub>2</sub> H <sub>4</sub> )ClSnFe (CO) <sub>2</sub> Cp	5	5
C <sub>2</sub> F <sub>5</sub> Fe (CO) <sub>2</sub> Cp	3	4
C <sub>3</sub> F <sub>7</sub> Fe (CO) <sub>2</sub> Cp	3	4

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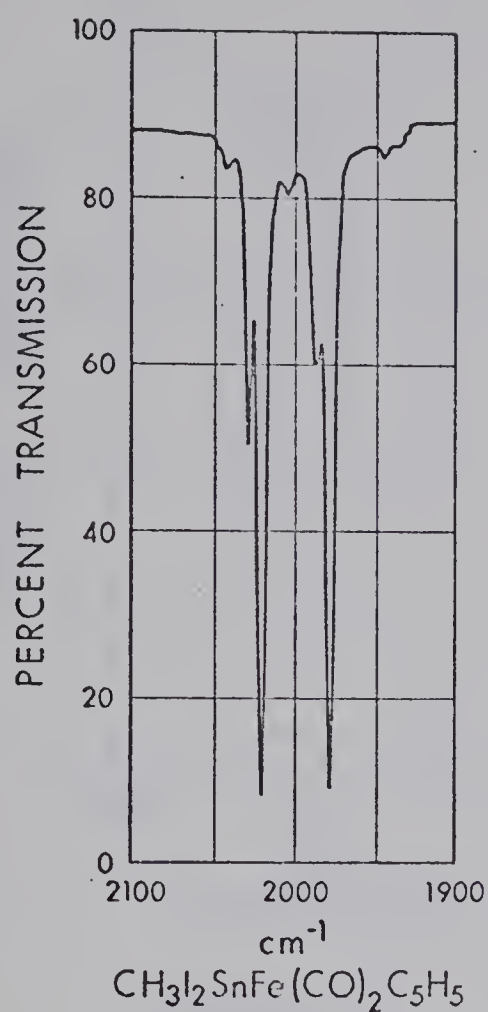


FIGURE 54

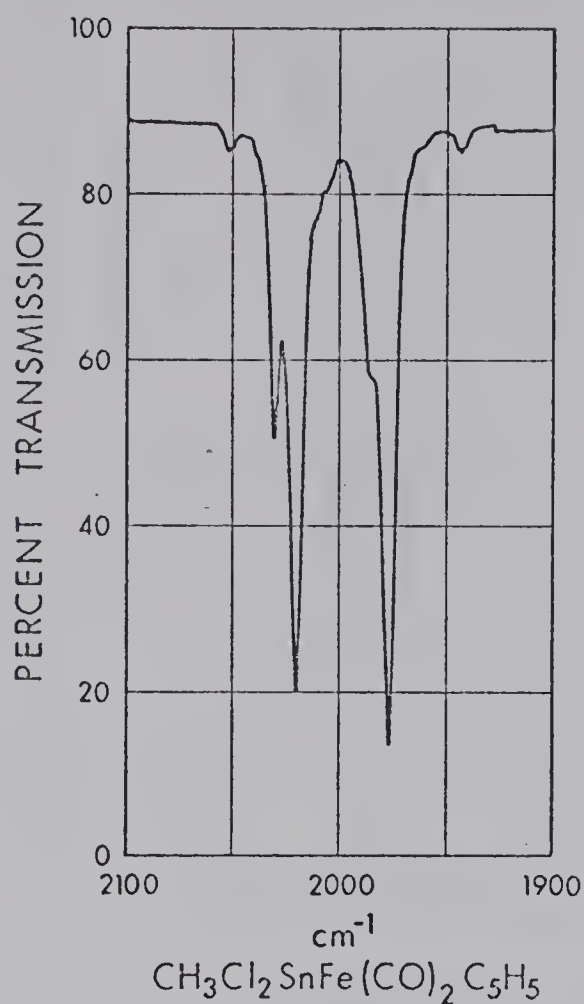


FIGURE 55

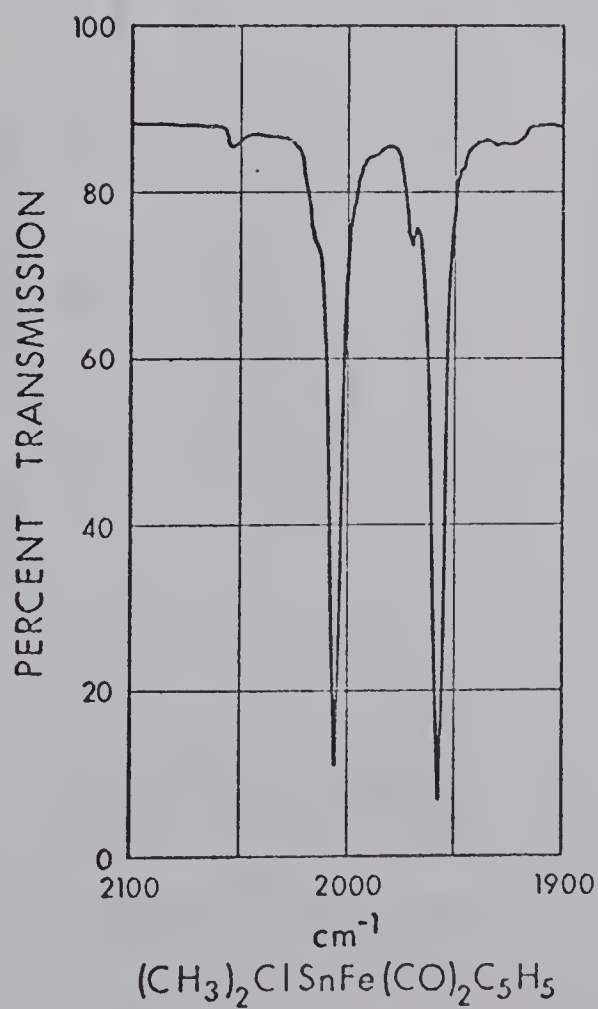


FIGURE 56

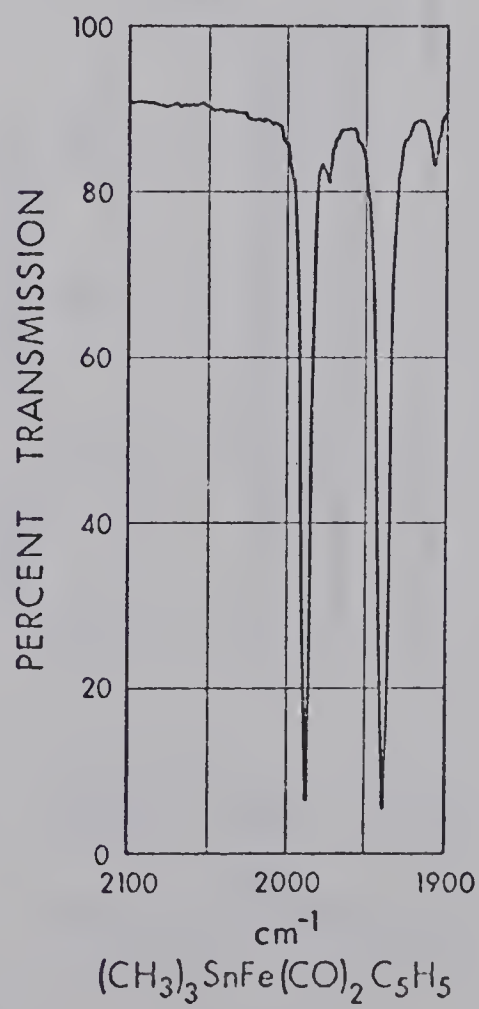


FIGURE 57



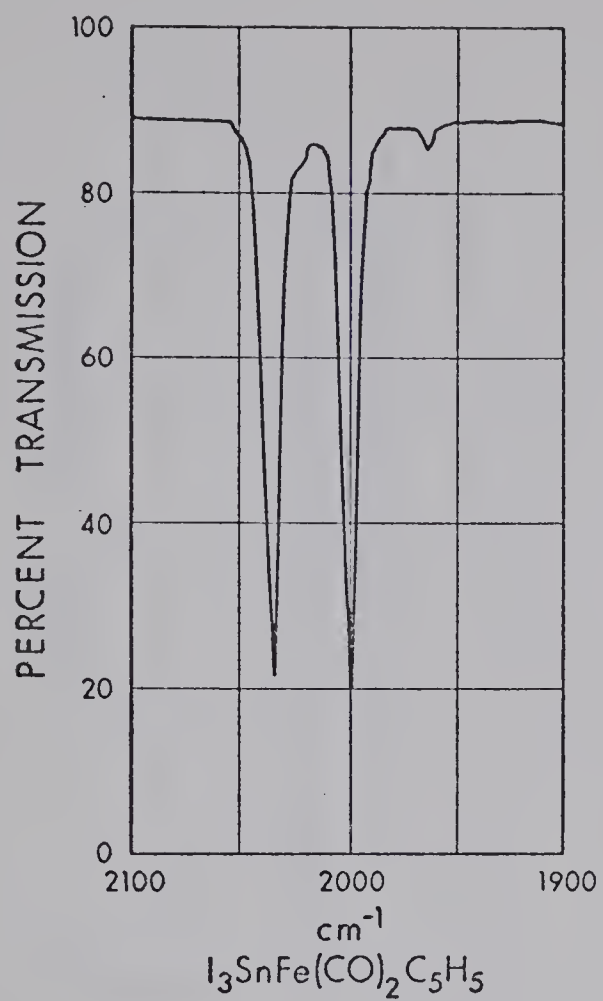


FIGURE 58

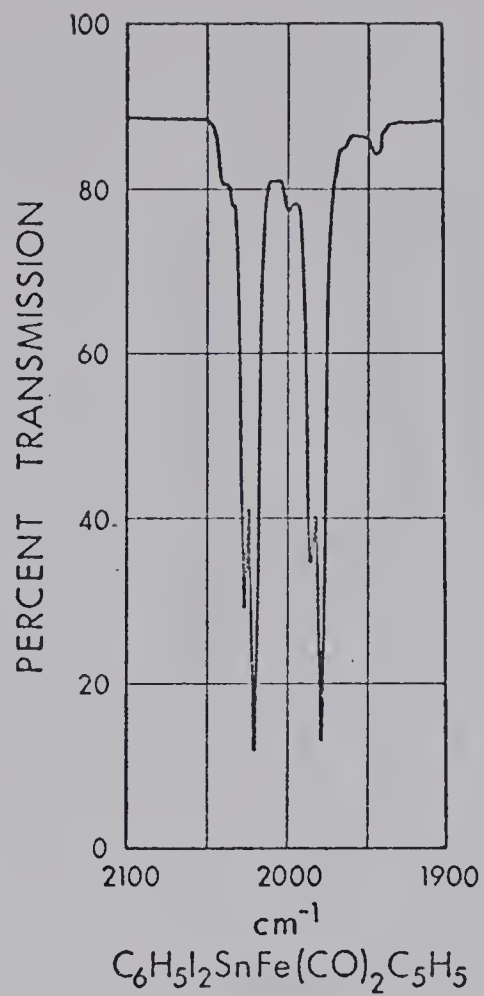


FIGURE 59

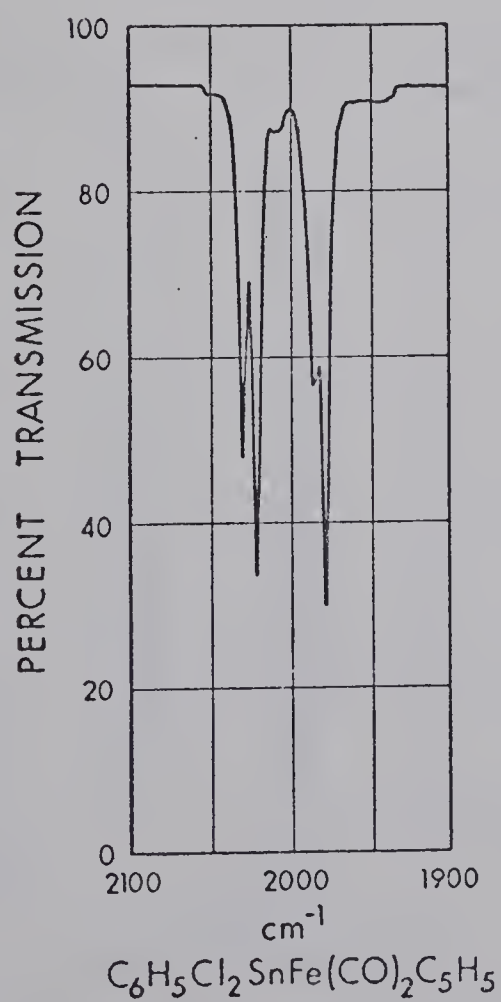


FIGURE 60

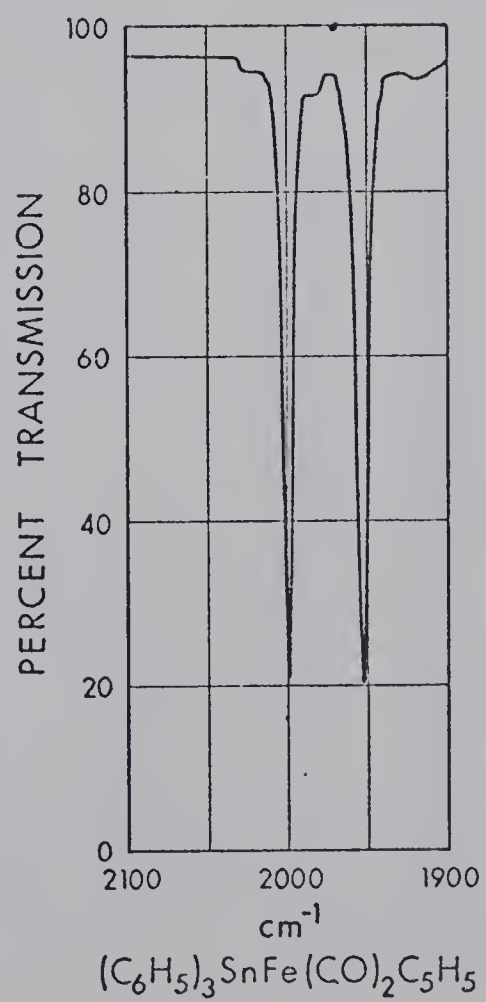


FIGURE 61



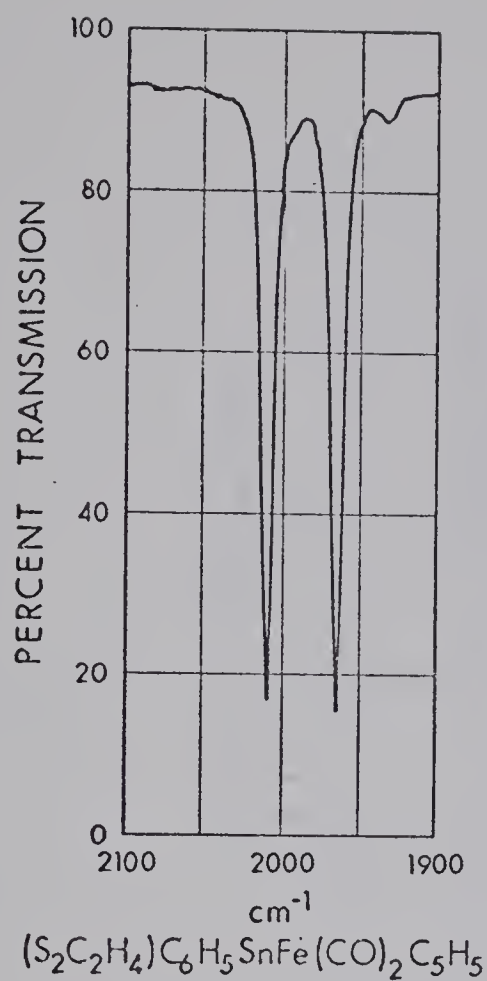


FIGURE 62

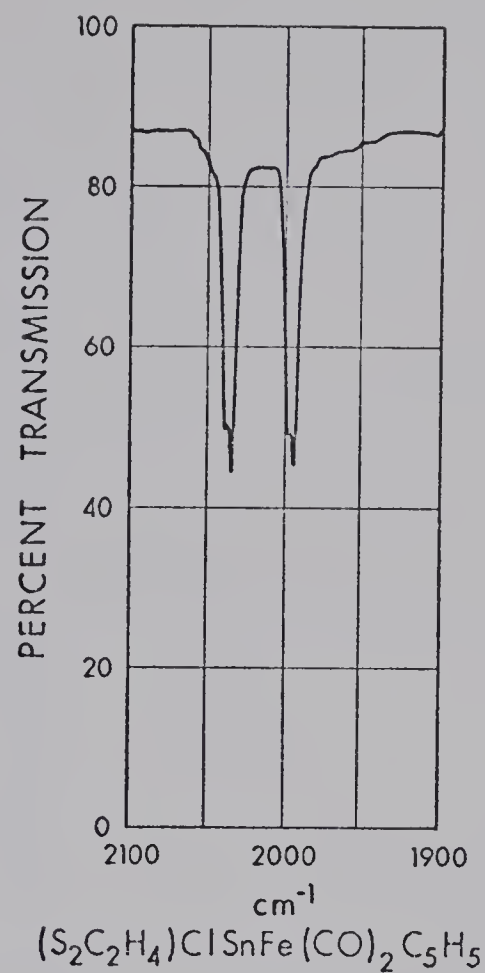


FIGURE 63

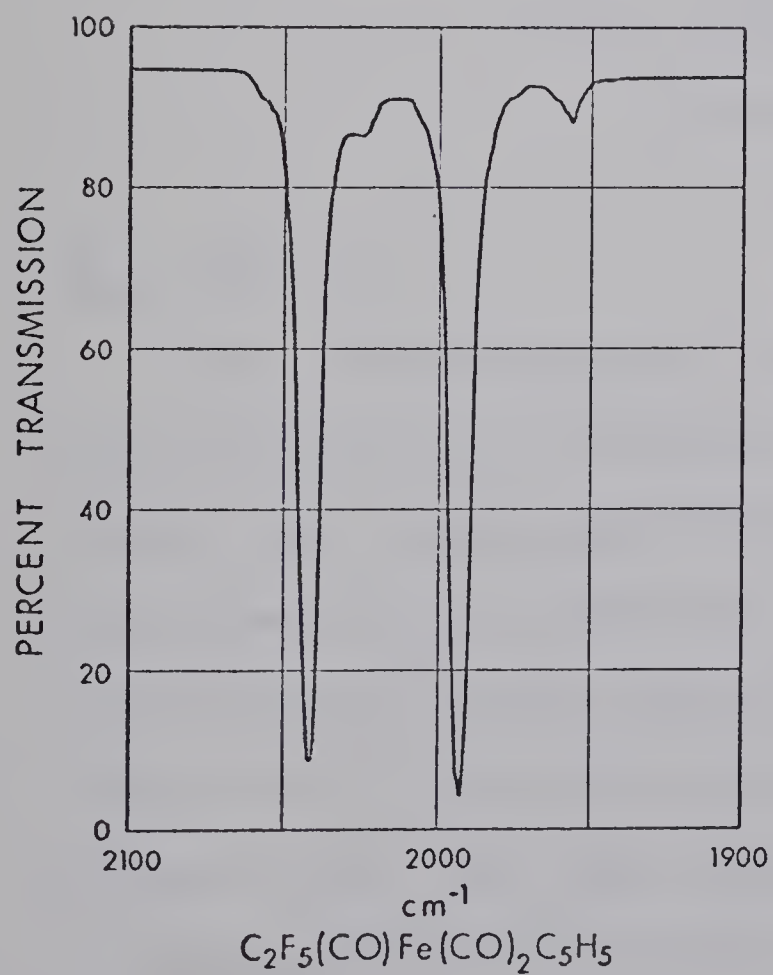


FIGURE 64

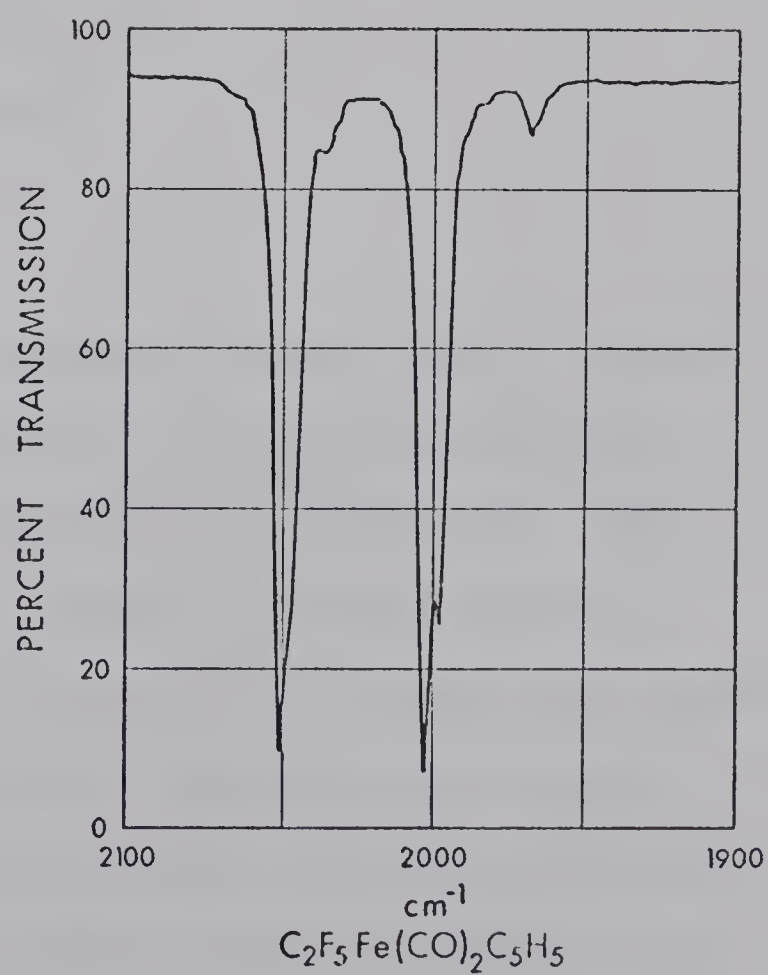


FIGURE 65



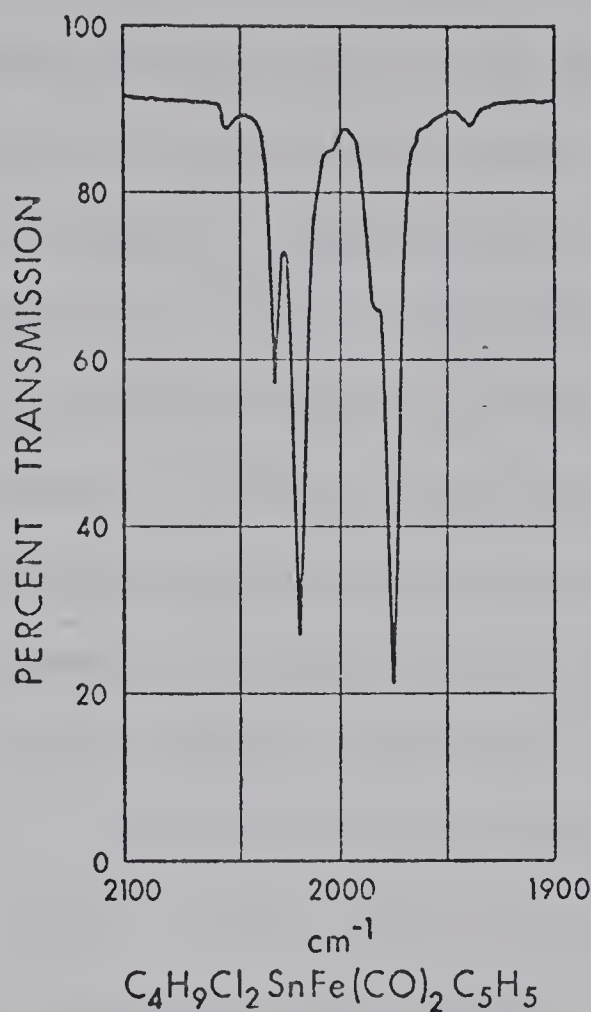


FIGURE 66

$(\Delta_1)$  and  $(\Delta_2)$ .

The electronegativity argument can be used to explain the differences in the spectra of  $(\text{S}_2\text{C}_2\text{H}_4)\text{ClSnFe(CO)}_2\text{Cp}$  (Figure 63) and  $(\text{S}_2\text{C}_2\text{H}_4)\text{PhSnFe(CO)}_2\text{Cp}$  (Figure 62). The electronegativity difference between chlorine and the  $\text{S}_2\text{C}_2\text{H}_4$  moiety appears large enough to give observable splittings ( $5\text{ cm}^{-1}$ ) while that between the phenyl and  $\text{S}_2\text{C}_2\text{H}_4$  groups is not, i.e. the carbonyl bands for both conformers in  $(\text{S}_2\text{C}_2\text{H}_4)\text{PhSnFe(CO)}_2\text{Cp}$  are close enough in energy to be undetectable. It appears that the electronegativity dif-





ference between fluorine and  $\text{CF}_3$  is large enough to give observable splittings of 3 and 4  $\text{cm}^{-1}$ .

Silicon derivatives such as  $\text{Ph}_2\text{HSiFe}(\text{CO})_2\text{Cp}$  and  $\text{PhH}_2\text{SiFe}(\text{CO})_2\text{Cp}$  have also been found to show no splitting of the carbonyl bands.<sup>1</sup> Derivatives with three different groups on the silicon such as  $\text{ClHMeSiFe}(\text{CO})_2\text{Cp}$  and  $\text{PhMeClSiFe}(\text{CO})_2\text{Cp}$  showed three and two pairs of carbonyl bands respectively.<sup>1</sup> These results are also consistent with the electronegativity argument given above.

The nmr spectra of  $\text{MeCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$  and  $\text{MeI}_2\text{SnFe}(\text{CO})_2\text{Cp}$  showed only singlet methyl resonances in the temperature range 30 to  $-50^\circ$ . Below  $-50^\circ$  solubility problems were encountered. Since the nmr time scale is  $10^8$  to  $10^{10}$  times slower than the infrared time scale, it appeared that interconversion between conformers was too rapid even at  $-50^\circ$ . Only an averaged methyl resonance would then be observed.

However, an alternate explanation can be put forth from the results of a recent low temperature infrared study on  $\text{MeCl}_2\text{GeFe}(\text{CO})_2\text{Cp}$  by Nesmeyanov et al.<sup>199</sup> At  $-40^\circ$  they observed the disappearance of two of the four carbonyl stretching bands. This implies that only one stable conformation exists at  $-40^\circ$ ; by lowering the temperature the higher energy conformer is depleted by the Boltzmann Principle before interconversion is slowed enough to be



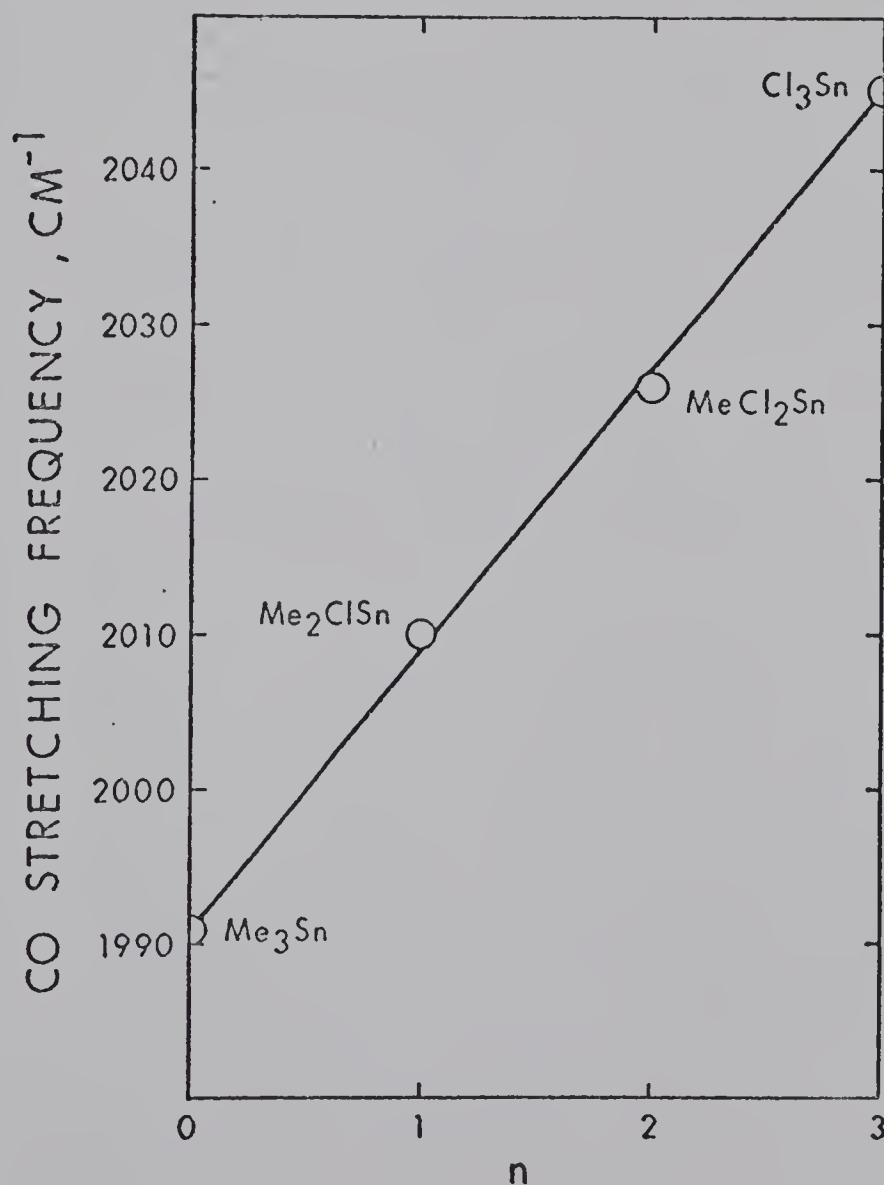
detected on the nmr time scale. Therefore, at best the nmr spectrum will show only a small shift in band position at low temperature.

Numerous other examples of conformational isomerism of this type have been observed from spectroscopic studies. Herber and Goscinny<sup>200</sup> have concluded from Mossbauer and infrared studies that conformational isomers exist for  $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]$ , and  $\text{Cl}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ . Compounds such as  $\text{Cl}_3\text{SiFe}(\text{CO})_2\text{CpMe}$ ,<sup>1</sup>  $\pi\text{-C}_3\text{H}_5\text{Mo}(\text{CO})_3\text{Cp}$ ,<sup>201,202</sup>  $\pi\text{-Ph}_3\text{C}_3\text{Co}(\text{CO})_3\text{PPhMe}$ ,<sup>203</sup>  $(\text{MeO})_3\text{SiFe}(\text{CO})_2\text{Cp}$ ,<sup>1</sup>  $(\text{MeCl}_2\text{Si})_2\text{Fe}(\text{CO})_4$ ,<sup>1</sup> all showed more carbonyl stretching bands in the infrared spectrum than carbonyl groups in the molecule. These can be explained by invoking conformational isomers similar to the ones discussed in this Chapter.

From force constant calculations on manganese pentacarbonyl derivatives, Graham has shown that various tin ligands act as  $\pi$ -acceptors to some extent. These  $\pi$ -accepting abilities were found to fall in a small region for a large variety of tin ligands. Therefore, the symmetric carbonyl stretching frequencies should be mainly a function of the  $\sigma$ -withdrawing ability of the tin ligand. Then the carbonyl stretching frequencies should be proportional to the sum of electronegativities of the ligands attached to the tin. (This assumes that  $\pi$ -bonding between the ligands and tin can be neglected).



If the R groups in  $R_3SnFe(CO)_2Cp$  are successively replaced by halogens, a linear relationship is observed by plotting the number of halogens vs the high energy (symmetric stretch) carbonyl band (averaged values were used in cases where band splittings were observed). This is illustrated in Figure 67 for the series where  $R = Me$ . Analogous relationships have been found for tin derivatives of manganese pentacarbonyl<sup>205</sup> and of cobalt tetracarbonyl.<sup>206</sup>



Plot of Symmetric CO Stretching Frequency vs n for the series



FIGURE 67





The nmr chemical shifts of the cyclopentadienyl protons for the tin complexes (see Table XXI) are consistent with the  $\sigma$ -withdrawing abilities of the tin ligands; stronger  $\sigma$ -withdrawers show lower chemical shifts.



## EXPERIMENTAL

A nitrogen atmosphere was maintained during reactions and work-up procedures mainly by the use of standard taper equipment.

Melting points, microanalytical results, infrared spectra, nmr spectra and mass spectra were obtained as previously described. Solution molecular weights were obtained in benzene using a Mechrolab Osmometer. Results are given in Table XX and XXI.

Samples of  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  were purchased from Strem Chemicals Inc., Danvers, Mass. and were recrystallized before use. The tin chlorides ( $\text{SnCl}_4$ ,  $\text{PhSnCl}_3$ ,  $\text{Ph}_2\text{SnCl}_2$ ,  $n\text{-BuSnCl}_3$ ,  $\text{MeSnCl}_3$ ,  $\text{Me}_2\text{SnCl}_2$ ,  $\text{Me}_3\text{SnCl}$ ,  $\text{Ph}_3\text{SnCl}$ ) were purchased from M and T Chemical Inc., and Alfa Inorganics. The perfluoro carbon compounds  $\text{C}_3\text{F}_7\text{COCl}$  and  $\text{C}_2\text{F}_5\text{COCl}$  were purchased from Peninsular Chemresearch, Gainesville, Florida. Tetrahydrofuran was freshly distilled from  $\text{LiAlH}_4$  prior to use. Silicic acid (Mallinckrodt AR100 mesh) was used in the chromatography columns. All other reagents and solvents were commercially available reagent grades and were used without further purification. Procedures are now given for the various compounds prepared.



TABLE XX

## ANALYTICAL DATA, COLORS AND MELTING POINTS OF TIN-IRON COMPOUNDS

Compound	mp Observed	Lit.	Color	Calculated %				Found %			
				C	H	O	Halogen	C	H	O	Halogen
$\text{Cl}_3\text{SnFe}(\text{CO})_2\text{Cp}$	155-157d	157d <sup>25</sup>	yellow								
$\text{I}_3\text{SnFe}(\text{CO})_2\text{Cp}$	117-119	119 <sup>64</sup>	orange								
$\text{PhCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	114-116	108 <sup>64</sup>	pale yellow	35.18	2.27	7.21	15.98	35.36	2.28	7.39	15.94
$\text{PhI}_2\text{SnFe}(\text{CO})_2\text{Cp}$	129-133	-	orange	24.91	1.61	5.11	40.51	25.11	1.56	5.30	40.83
$\text{MeCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	113-115	-	pale yellow	25.19	2.11	8.39	18.58	25.03	2.24	8.62	18.45
$\text{MeI}_2\text{SnFe}(\text{CO})_2\text{Cp}$	141-144	-	yellow orange	17.01	1.43	5.66	44.92	17.17	1.36	5.75	45.24
$n\text{-BuCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	42-43	-	pale yellow	31.18	3.30	7.57	16.73	31.02	3.49	7.69	16.71
$\text{Me}_2\text{ClSnFe}(\text{CO})_2\text{Cp}$	45-46	-	pale yellow	29.93	3.07	8.85	9.82	30.15	3.21	8.93	9.66
$(\text{S}_2\text{C}_2\text{H}_4)\text{ClSnFe}(\text{CO})_2\text{Cp}$	113-117	-	bright yellow	25.54	2.14	15.16(s)	8.38	25.33	2.17	15.37(s)	8.20
$\text{Ph}(\text{S}_2\text{C}_2\text{H}_4)\text{SnFe}(\text{CO})_2\text{Cp}$	110-111	-	yellow	38.74	3.04	6.88	13.80(s)	38.70	3.06	7.03	13.96(s)
$\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}$	138-141	139-141 <sup>25</sup>	pale yellow	-	-	-	-	-	-	-	-
$\text{Me}_3\text{SnFe}(\text{CO})_2\text{Cp}$	liquid	liquid <sup>195</sup>	yellow	35.25	4.14	-	-	35.29	4.51	-	-



TABLE XX (continued)

$C_3F_7Fe(CO)_2Cp$	liquid	31-32 <sup>197</sup>	orange	34.71	1.46	-	38.44	35.55	1.45	-	37.15
$C_2F_5Fe(CO)_2Cp$	42-45	43-45 <sup>197</sup>	orange	36.52	1.70	-	-	36.22	1.78	-	-
$C_3F_7COFe(CO)_2Cp$	liquid	liquid <sup>197</sup>	orange	35.32	1.35	-	35.56	35.66	1.58	-	37.57
$C_2F_5COFe(CO)_2Cp$	53-57	54-57 <sup>197</sup>	orange	37.08	1.56	-	-	37.22	1.77	-	-





TABLE XXI

## INFRARED CARBONYL STRETCHING FREQUENCIES AND NMR DATA OF TIN-IRON COMPOUNDS

Compound	Carbonyl Stretching Frequencies (cm <sup>-1</sup> ) <sup>a</sup>	Molecular Weights		Nmr τ (Cp) <sup>c</sup>
		Calc.	Found <sup>b</sup>	
Cl <sub>3</sub> SnFe(CO) <sub>2</sub> Cp	2045(9.6) 2006(10.0)	-	-	4.77
I <sub>3</sub> SnFe(CO) <sub>2</sub> Cp	2036(9.7) 2000(10.0)	-	-	-
PhCl <sub>2</sub> SnFe(CO) <sub>2</sub> Cp	2032(7.3) 1980(10.0) 1987(5.9)	444	447	4.85
PhI <sub>2</sub> SnFe(CO) <sub>2</sub> Cp	2027(7.7) 2020(10.0) 1978(9.9)	627	648	4.98
MeCl <sub>2</sub> SnFe(CO) <sub>2</sub> Cp	2031(5.2) 2021(9.2) 1978(10.0)	382	374	4.88
MeI <sub>2</sub> SnFe(CO) <sub>2</sub> Cp	2027(4.5) 2017(10.0) 1976(9.9)	565	580	5.03
n-BuCl <sub>2</sub> SnFe(CO) <sub>2</sub> Cp	2029(5.0) 2019(9.2) 1974(10.0)	424	459	-
Me <sub>2</sub> ClSnFe(CO) <sub>2</sub> Cp	2015(1.9 sh) 2006(9.4) 1958(10.0)	-	-	5.09
(S <sub>2</sub> C <sub>2</sub> H <sub>4</sub> )ClSnFe(CO) <sub>2</sub> Cp	2033(8.5) 2028(10.0) 1987(9.6)	423	440	4.86
Ph(S <sub>2</sub> C <sub>2</sub> H <sub>4</sub> )SnFe(CO) <sub>2</sub> Cp	2011(9.6) 1967(10.0)	-	-	-
Ph <sub>3</sub> SnFe(CO) <sub>2</sub> Cp	1998(9.8) 1952(10.0)	-	-	5.26
Me <sub>3</sub> SnFe(CO) <sub>2</sub> Cp	1991(9.8) 1941(10.0)	-	-	5.31



TABLE XXI (continued)

$C_3F_7Fe(CO)_2Cp$	2050 (9.5) 1999 (8.0)	2047 (8.3 sh)	2003 (10.0)	346	340	-
$C_2F_5Fe(CO)_2Cp$	2051 (9.4) 1999 (8.1)	2048 (8.5 sh)	2003 (10.0)	296	310	4.97
$C_3F_7COFe(CO)_2Cp$	2044 (9.3)	1997 (10.0)	-	-	-	-
$C_2F_5COFe(CO)_2Cp$	2044 (9.4)	1996 (10.0)	-	324	320	4.98

<sup>a</sup> Cyclohexane solutions. Figure in parenthesis are relative intensities on a transmittance scale; sh = shoulder.

<sup>b</sup> In benzene solution by osmometric method.

<sup>c</sup> In  $CDCl_3$  solutions.



Methyldichlorotin( $\pi$ -cyclopentadienyl)dicarbonyliron,



A magnetically stirred mixture of  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  (3.97 g, 11.2 mmol) and  $\text{MeSnCl}_3$  (2.58 g, 10.8 mmol) in 70 ml methylcyclohexane was heated at 95-100° for 15 hours. After removing solvent at reduced pressure, the residual material was chromatographed on 100 grams silicic acid ( $\text{CHCl}_3$  elution). The order of elution and the amounts of each compound obtained were as follows:

(1)	$[\text{Fe}(\text{CO})_2\text{Cp}]_2$	0.87 g
(2)	$\text{MeCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$	1.20 g
(3)	$\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$	0.38 g
(4)	$\text{ClFe}(\text{CO})_2\text{Cp}$	1.16 g

Fraction (2) was recrystallized from hexane-dichloromethane to afford pale-yellow crystals of the product (0.90 g).

Complexes  $\text{Cl}_3\text{SnFe}(\text{CO})_2\text{Cp}$ ,  $\text{PhCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$ ,  $n\text{-BuCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$ ,  $\text{Me}_2\text{ClSnFe}(\text{CO})_2\text{Cp}$ .

These compounds were prepared from the appropriate tin chloride and  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  in an analogous manner to that given above for  $\text{MeCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$ . Separation of products was by chromatography; products eluted through the column immediately after  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  except for  $\text{Me}_2\text{ClSnFe}(\text{CO})_2\text{Cp}$ , which was eluted just before  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ .



The reaction conditions and yields were given in Table XVIII.

Methyldiiodotin( $\pi$ -cyclopentadienyl)dicarbonyliron,  
 $\text{MeI}_2\text{SnFe}(\text{CO})_2\text{Cp}$ .

A 25 ml acetone solution of  $\text{MeCl}_2\text{SnFe}(\text{CO})_2\text{Cp}$  (0.32 g, 0.84 mmol) and sodium iodide (0.28 g, 1.84 mmol) was stirred at room temperature for three hours. The white precipitate of NaCl was filtered off and the filtrate was evaporated down at reduced pressure. Recrystallization of the orange residue from dichloromethane-hexane afforded yellow-orange crystals (0.40 g, 84%) of  $\text{MeI}_2\text{SnFe}(\text{CO})_2\text{Cp}$ .

Complexes  $\text{I}_3\text{SnFe}(\text{CO})_2\text{Cp}$  and  $\text{PhI}_2\text{SnFe}(\text{CO})_2\text{Cp}$ .

These two compounds were obtained from their respective chlorides and sodium iodide as described above for  $\text{MeI}_2\text{SnFe}(\text{CO})_2\text{Cp}$ .

[Chloro(ethanedithiolato)tin]( $\pi$ -cyclopentadienyl)dicarbonyliron,  $(\text{S}_2\text{C}_2\text{H}_4)\text{ClSnFe}(\text{CO})_2\text{Cp}$ .

Addition of 1 ml of triethylamine to a 25 ml benzene solution containing  $\text{Cl}_3\text{SnFe}(\text{CO})_2\text{Cp}$  (2.09 g, 5.20 mmol) and 1,2-ethanedithiol (0.40 ml, 4.07 mmol) gave an immediate precipitate of  $\text{Et}_3\text{NHCl}$ . Stirring was continued for one hour to ensure completion of reaction. The mixture was filtered and the filtrate was evaporated down at reduced pressure





leaving a yellow solid. Two recrystallizations from hexane-dichloromethane afforded bright-yellow crystals of the product (2.00 g).

Complex  $(S_2C_2H_4)PhSnFe(CO)_2Cp$ .

This complex was obtained in 60% yield from  $PhCl_2SnFe(CO)_2Cp$  and  $HS-(CH_2)_2-SH$  from a procedure analogous to that described above for  $(S_2C_2H_4)ClSnFe(CO)_2Cp$ .

Complexes  $Ph_3SnFe(CO)_2Cp$  and  $Me_3SnFe(CO)_2Cp$ .

These two compounds were prepared from  $[Fe(CO)_2Cp]^\ominus$  and  $R_3SnCl$  following the procedure reported by Gorsich.<sup>25</sup>

Complexes  $C_3F_7COFe(CO)_2Cp$ ,  $C_2F_5COFe(CO)_2Cp$ ,  $C_3F_7Fe(CO)Cp$ ,  $C_2F_5Fe(CO)_2Cp$ .

These compounds were prepared according to the procedures given by King and Bisnette.<sup>197</sup>



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